PREPARATION AND REACTIONS OF PARTIALLY FLUORINATED DIENES

BY

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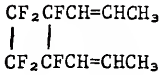

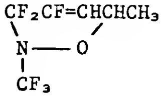

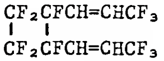

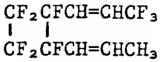

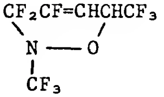

Abstract of Dissertation Presented to the Graduate Council
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Doctor of Philosophy

PREPARATION AND REACTIONS OF PARTIALLY FLUORINATED DIENES

By

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December 1980

Chairman: Dr. Paul Tarrant
Major Department: Department of Chemistry

The preparation of three fluorine-containing dienes, 1,1,2-trifluoropentadiene-1,3 (I), 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II), and 1,4-perfluoropentadiene (III) was carried out. Two asymmetric centers present in the precursors of I and II, $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (IV) and $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ (V), made possible the separation of two diastereomers for each alkane. The dehydrohalogenation reaction of IV and V with ethanolic potassium hydroxide gave exclusively the trans products, $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$ (VI) and $CF_2Cl\overset{*}{C}FClCH{=}CHCF_3$ (VII). The products realized by dehalogenation of VI and VII with zinc were the respective dienes I and II. The 1,4-perfluoropentadiene was prepared by the decarboxylation reaction of $CF_2ClCFBrCF_2CFBrCF_2COONa$ to give the olefin $CF_2ClCFBrCF_2CF{=}CF_2$, which was dehalogenated with zinc to give the diene III.

Three types of reactions were studied with the dienes, 2 + 2 cycloaddition, nucleophilic addition, and radical addition. The formation of a cyclobutane product from I at 0°C indicated the unusual reactivity of this diene. At a temperature of 100°C, both I and II reacted quantitatively in 20 hours to give the respective cyclobutane products. The reaction of a mixture of I and II at 100°C gave an almost statistical distribution of the two homo-cyclobutane products along with the mixed cyclobutane. The attempt to form cyclobutane products from 1,4-perfluoropentadiene was unsuccessful.

Nucleophilic addition reactions using phenylmagnesium bromide and ethanolic potassium hydroxide with I gave the addition-elimination product and products formed by 1,2 and 1,4 addition, respectively. Reaction of II with phenylmagnesium bromide resulted in the addition-elimination product. Alcohol added 1,4 to give the ether.

Three types of radical initiated reactions were studied with the dienes. Trifluoronitrosomethane reacted with I and II, respectively, to give the Diels-Alder products and polymer products which contained both 1,2 and 1,4 structural units. No reaction took place between III and CF_3NO. The addition of bromine to I gave only the 1,2 adduct. Diene II reacted with bromine to give both 1,2 and 1,4 addition products. 1,4-Perfluoropentadiene reacted with bromine to give 1,2 addition product with no cyclization products detected. Bromotrichloromethane gave the simple 1 to 1 adduct with diene I and higher telomers with no 1 to 1 adduct structure for II. Diene III did not react with CCl_3Br.

Eight new compounds were prepared and characterized by infrared analysis, NMR, and mass spectral data.

SECTION 1

INTRODUCTION

Preparation of Olefins

A number of reports has appeared in the literature on the preparation and reaction of haloalkanes to give fluorine-containing enes and dienes. Very little information, however, has been made available on the study of the reactions of 1,1,2-trifluoro-dienes.

Hexafluorobutadiene-1,3, because of its availability, has been historically the most studied of the fluorine-containing diene compounds. Examples of polymerization reactions involving homo-polymers, co-polymers, and ter-polymers of hexafluorobutadiene-1,3 are prevalant in literature reports.

The preparations of fluorine-containing dienes have been reported by several groups.[1-3] A general method for the preparation of these compounds can be shown as follows:

1. $XCF_2CFYZ + CH_2{=}CHR \longrightarrow CF_2X\overset{*}{C}FYCH_2\overset{*}{C}HZR$

   $X = Cl, Br;\ Y = Cl;\ Z = Br, I;\ R = CH_3, CF_3$

2. $CF_2X\overset{*}{C}FYCH_2\overset{*}{C}HZR \xrightarrow[EtOH]{KOH} CF_2X\overset{*}{C}FYCH{=}CHR$

3. $CF_2X\overset{*}{C}RYCH{=}CHR \xrightarrow[EtOH]{Zinc} CF_2{=}CFCH{=}CHR$

The free radical addition reactions, involving halogen-containing compounds to olefins, have been used extensively to prepare fluoroalkanes.[1,2,4-10] The dehydrohalogenation is facilitated with potassium hydroxide and ethanol since the adjacent halogens cause the hydrogen to be more acidic than in hydrocarbon surroundings. Dehalogenation with zinc in ethanol is common for the preparation of fluorinated olefins.

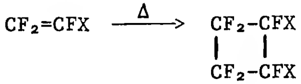
The usual reactions of fluoroalkenes such as halogen addition, radical initiated additions, nucleophilic attack, and 2 + 2 cycloadditions, have not been thoroughly studied for 1,1,2-trifluorodienes. The lack of activity in this area prompted our research.

Reactions of Olefins

2 + 2 Cycloaddition Reactions

Fluorinated olefins usually give 2 + 2 cycloaddition products when treated thermally as shown below:

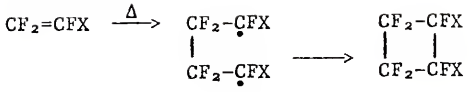
4.



$$CF_2{=}CFX \xrightarrow{\Delta} \begin{array}{l} CF_2-CFX \\ \;|\qquad\;\; | \\ CF_2-CFX \end{array}$$

X = Cl, F, Br, I, OCH_3, etc.

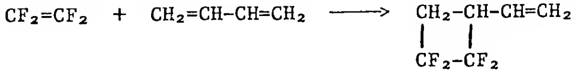
The 2 + 2 cycloaddition reaction has been mechanistically shown to be a two-step bi-radical process.[11]

5. 

$$CF_2{=}CFX \xrightarrow{\Delta} \begin{array}{l} CF_2-\underset{\bullet}{C}FX \\ | \\ CF_2-\underset{\bullet}{C}FX \end{array} \longrightarrow \begin{array}{l} CF_2-CFX \\ |\qquad | \\ CF_2-CFX \end{array}$$

X = F, Cl, Br, I, OCH_3, etc.

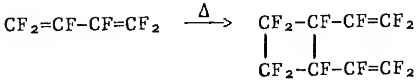
Those olefins which are very reactive in forming 2 + 2 cycloaddition products usually give no 2 + 4 Diels-Alder products. For example, tetrafluoroethylene reacts with butadiene to give only the vinylcyclobutane.[11]

6. 

$$CF_2{=}CF_2 + CH_2{=}CH-CH{=}CH_2 \longrightarrow \begin{array}{l} CH_2-CH-CH{=}CH_2 \\ |\qquad | \\ CF_2-CF_2 \end{array}$$

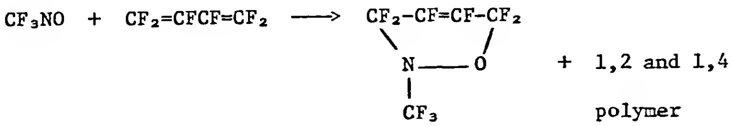
Diels-Alder products are only isolated from reactions where the diene is locked into a cisoid configuration such as cyclic dienes. Cyclopentadiene is one of the few dienes which form Diels-Alder products with fluoroolefins. A good review of Diels-Alder reactions of organic fluorine compounds can be found in Fluorine Chemistry Reviews, Vol. 1, No. 2.[12]

Hexafluorobutadiene-1,3 has been described as acting neither as the diene nor dienophile in a Diels-Alder reaction.

7. 

$$CF_2{=}CF-CF{=}CF_2 \xrightarrow{\Delta} \begin{array}{l} CF_2-CF-CF{=}CF_2 \\ |\qquad | \\ CF_2-CF-CF{=}CF_2 \end{array}$$

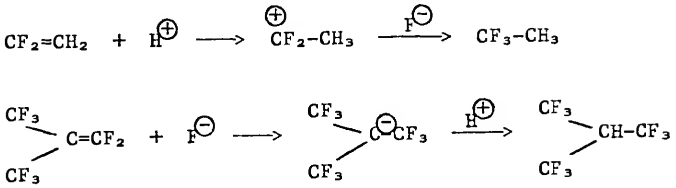
The only product isolated as the 2 + 4 Diels-Alder adduct with this diene has been that derived from trifluoronitrosomethane. Trifluoronitrosomethane has been reported to react with fluorinated dienes via a radical anion mechanism, probably involving $CF_3N(\overset{\ominus}{O})\dot{N}(O)-CF_3$.[13] The reaction with hexafluorobutadiene-1,3 gives the 2 + 4 Diels-Alder adduct along with polymeric products.

8.


The study of 2 + 2 cycloaddition reactions of fluorine-containing dienes, other than hexafluorobutadiene-1,3, has been neglected by previous workers.

Nucleophilic Reactions

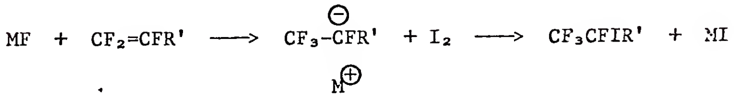
Most reactions involving fluorine-containing olefins are nucleophilic in nature, due to the stabilization of the anion by the halogen atoms in the α or β-position. Hydrocarbon and partially fluorinated olefins undergo electrophilic reactions because of stabilization of the intermediate positive charge. The higher the degree of fluorination the more likely the nucleophilic reaction to predominate, as the example shows.

9.


Fluorine-containing olefins are very susceptible to attack by nucleophiles such as Grignard reagents, alkoxides, and halide anions.[14-17] Examples of these reactions are as follows:

10. $RMgX + CF_2{=}CFR' \longrightarrow RCF{=}CFR' + MgXF$

11. $RO^{\ominus} + CF_2{=}CF_2 \xrightarrow{ROH} ROCF_2CF_2H + ROCF{=}CF_2$

12. 

$$MF + CF_2{=}CFR' \longrightarrow \underset{M^{\oplus}}{CF_3\text{-}\overset{\ominus}{C}FR'} + I_2 \longrightarrow CF_3CFIR' + MI$$

R = alkyl, aryl

R' = F, Cl, R_f, etc.

M = Na, K, Cs

The reactivities toward nucleophiles of dienes which contain fluorine vary. Tarrant and Heyes[15] found that Grignard reagents such as allylmagnesium bromide did not react with fluorinated dienes such as 1,1,2-trifluoropentadiene-1,4. The usual reaction of Grignard reagents gives the olefin by loss of fluoride ion.

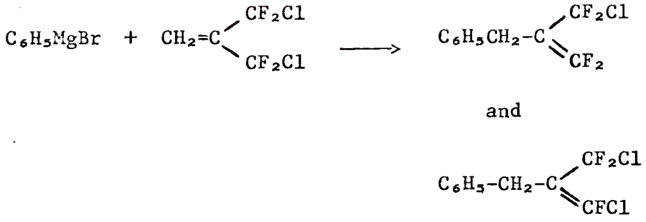
The addition-elimination or S_N2' type reaction of Grignard reagents with fluorinated olefins is well documented.[18] Rearrangements of the intermediate anion have been reported,[19] with the conjugated olefin predominating where possible.

13. $C_6H_5MgBr + CF_2{=}CFCF_2Cl \longrightarrow C_6H_5CF{=}CF\text{-}CF_2Cl$ predominant product

and

$C_6H_5CF_2\text{-}CF{=}CF_2$

14.



$$C_6H_5MgBr + CH_2{=}C\begin{smallmatrix}CF_2Cl\\CF_2Cl\end{smallmatrix} \longrightarrow C_6H_5CH_2{-}C\begin{smallmatrix}CF_2Cl\\ \| \\ CF_2\end{smallmatrix}$$

and

$$C_6H_5{-}CH_2{-}C\begin{smallmatrix}CF_2Cl\\ \| \\ CFCl\end{smallmatrix}$$

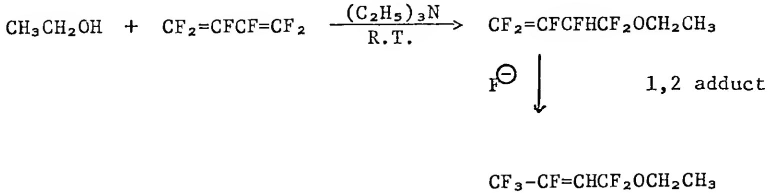
The reaction of alkyl Grignard reagents with olefins which contain fluorine has been shown by Okukara[14] to give two products.

15. $$CH_3CH_2MgX + CF_2{=}CCl_2 \longrightarrow \underset{\text{predominant product}}{CH_3CH_2{-}CF_2{-}CCl_2H} + CH_3CH_2{-}CF{=}CCl_2$$

A radical intermediate, not hydrolysis of the intermediate $CH_3CH_2CF_2CCl_2MgX$, was proposed to account for the formation of the major product.

Nucleophiles such as ethoxide ($CH_3{-}CH_2{-}O^{\ominus}$) have been added to hexafluorobutadiene-1,3 to give several products depending on reaction conditions. Knunyants et al.[20,21] reported the following sequence:

16.



$$CH_3CH_2OH + CF_2{=}CFCF{=}CF_2 \xrightarrow[\text{R.T.}]{(C_2H_5)_3N} CF_2{=}CFCFHCF_2OCH_2CH_3 \quad \text{1,2 adduct}$$

$$\downarrow F^{\ominus}$$

$$CF_3{-}CF{=}CHCF_2OCH_2CH_3$$

The allylic rearrangement of the fluoroether was unexpected for this type of unsaturated compound, but it was probably caused by the attack of fluoride anion, obtained from the partial hydrolysis of the ether, followed by the rearrangement and loss of fluoride. The same group also found that at higher temperatures, 90-100°C, the 1,4 addition product was obtained.

17. $CH_3CH_2OH + CF_2{=}CFCF{=}CF_2 \xrightarrow[90\text{-}100^\circ C]{(C_2H_5)_3N} CH_3CH_2OCF_2CF{=}CFCF_2H$

1,4 adduct

Dedek and Kovac[22] reported the following results from the reaction of ethanol and sodium ethoxide with hexafluorobutadiene-1,3.

18. $CH_3CH_2OH + CH_3CH_2ONa + CF_2{=}CFCF{=}CF_2 \longrightarrow$

$CH_3CH_2OCF_2CF{=}CHCOOCH_2CH_3$

Their product probably arose by the following reactions.

19. $CF_2{=}CFCF{=}CF_2 + CH_3CH_2OH \xrightarrow{CH_3CH_2ONa} CH_3CH_2OCF_2CFHCF{=}CF_2$

20. $CH_3CH_2OCF_2CFHCF{=}CF_2 + CH_3CH_2OH \longrightarrow CH_3CH_2OCF_2CFHCFHCF_2OCH_2CH_3$

21. $CH_3CH_2OCF_2CFHCFHCF_2OCH_2CH_3 \xrightarrow{-HF} CH_3CH_2OCF_2CF{=}CHCF_2OCH_2CH_3$

$\downarrow$ hydrolysis

$CH_3CH_2OCF_2CF{=}CHCOOCH_2CH_3$

The various results were ascribed to temperature dependence and base strength differences. The addition of alcohols to fluorine-containing conjugated triene systems has also been studied by Dedek and Kovac[22] and results in addition-elimination reaction to give the α,ω-triene diether.

22. $CF_2{=}CFCF{=}CFCF{=}CF_2 + CH_3CH_2OH + CH_3CH_2ONa \longrightarrow$

$CH_3CH_2OCF{=}CFCF{=}CFCF{=}CFOCH_2CH_3$

The study of nucleophilic attack on fluorinated 1,1,2-trifluorodiene systems has not been reported except for isolated cases such as fluoride anion induced rearrangement of perfluorinated compounds.[23,24]

23. $CF_2{=}CFCF{=}CFCF_3 + CsF \longrightarrow CF_3C{\equiv}CCF_2CF_3$

Radical Reactions

Halogen atoms are added to the double bonds of fluorinated olefins by radical means.[24] Electrophilic ionic additions such as occur in hydrocarbon olefins are rare but do occur in olefins which contain both hydrogen and fluorine. In the fluorine-containing 1,1,2-trifluoro-dienes we propose to study, two products can be formed.

24. $CF_2{=}CF{-}CH{=}CHR + Br_2 \longrightarrow CF_2Br{-}CFBr{-}CH{=}CHR$ 1,2 adduct

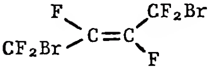
and

$CF_2Br{-}CF{=}CH{-}CHBrR$ 1,4 adduct

$R = CH_3, CF_3$

Study of halogen addition to fluorinated conjugated dienes has been limited to selected dienes such as hexafluorobutadiene-1,3, 1,1,2-trifluorobutadiene-1,3, and 1,1,2,4-tetrafluorobutadiene-1,3. Rondarev et al.[25] proposed an ionic mechanism in the bromination of the selected dienes. From hexafluorobutadiene-1,3, the (E)-1,4-dibromoperfluoro-2-butene was formed exclusively.

25. $CF_2{=}CFCF{=}CF_2 + Br_2 \longrightarrow$

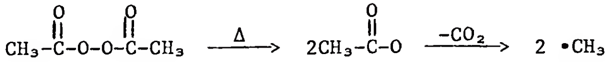


The 1,4-addition product was also obtained in the reaction of iodine monochloride with the butadienes and an ionic mechanism was proposed.[25]

26. $ICl + CF_2{=}CF{-}CH{=}CH_2 \longrightarrow CF_2ClCF{=}CHCH_2I$

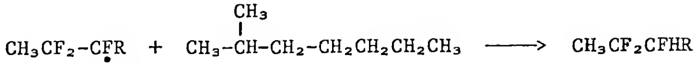
A good review of reactions between fluoroolefins and electrophiles can be found in <u>Fluorine Chemistry Reviews</u>, Vol. 3.[26]

Other results involving hydrocarbon radical reactions with fluorinated dienes have shown that dienes such as hexafluorobutadiene-1,3 are more reactive than mono-olefins. The difference in reactivity, however, is not so great as in the corresponding hydrocarbon systems. Sass et al.[10] found the reactivity of radicals with fluorinated olefins to decrease according to the following substitution pattern: $CF_2=CF_2 > CF_2=CFOR > CF_2=CFR_f$. He carried out the addition of methane to the alkenes by the reactions shown below:

27. 

$$CH_3-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\Delta} 2CH_3-\overset{O}{\overset{\|}{C}}-O \xrightarrow{-CO_2} 2\ \bullet CH_3$$

28. $\bullet CH_3 + CF_2=CFR \longrightarrow CH_3-CF_2-\underset{\bullet}{C}FR$

29. 

$$CH_3CF_2-\underset{\bullet}{C}FR + CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_2CH_2CH_2CH_3 \longrightarrow CH_3CF_2CFHR$$

$R = F$, OR or R_f

Halogen addition reactions and polymerizations are the only types of radical reactions which have been reported for conjugated 1,1,2-trifluoro-dienes except for the isolated case where Muramatsu added bromotrichloromethane to $CF_2=CFCH=CH_2$.[8]

Muramatsu and Tarrant[8] studied the radical addition of bromotrichloromethane to 1,1,2-trifluorobutadiene and the non-conjugated 1,1,2-trifluoropentadiene-1,4. The attack on the hydrocarbon segment of the dienes was unexpected.

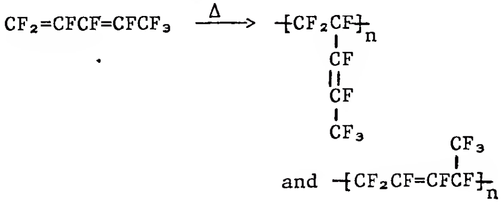
30. $CCl_3Br + CF_2=CFCH=CH_2 \longrightarrow CCl_3CH_2CH=CFCF_2Br$ and polymer by 1,4 addition

31. $CCl_3Br + CF_2{=}CFCH_2CH{=}CH_2 \longrightarrow CCl_3CH_2\overset{*}{C}HBrCH_2CF{=}CF_2$

and

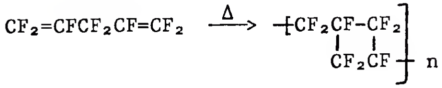
$CCl_3CH_2\overset{*}{C}HBrCH_2\overset{*}{C}FBrCF_2CCl_3$

Polymerization of conjugated dienes gives polymers of both 1,2 and 1,4 structure. The polymerizations proceed by a radical mechanism.[27,28]

32.


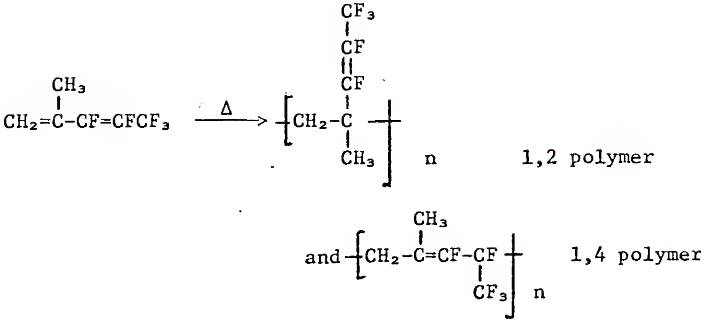
$$CF_2{=}CFCF{=}CFCF_3 \xrightarrow{\Delta} \left[CF_2\underset{\underset{\underset{CF_3}{|}}{\overset{\|}{CF}}}{\underset{|}{CF}}\right]_n \text{ and } \left[CF_2CF{=}CF\overset{\overset{CF_3}{|}}{C}F\right]_n$$

Non-conjugated perfluorodienes are reported to give intramolecular cyclic polymers.[29-35]

33.


According to Muramatsu et al.[4] even hindered partially fluorinated pentadienes such as 2-methyl-3,4,5,5,5-pentafluoro-1,3-pentadiene polymerized to give both 1,2 and 1,4 polymer structures. Muramatsu obtained polymers which contained both vinyl side chains and double bonds in the backbone of the polymer.

34.



$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CF{=}CFCF_3 \xrightarrow{\Delta} \left[CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\overset{\overset{\overset{\displaystyle CF_3}{|}}{CF}}{\|}}{\overset{CF}{|}}}{C}} \right]_n \quad \text{1,2 polymer}$$

$$\text{and} \left[CH_2{-}\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CF{-}\underset{\underset{\displaystyle CF_3}{|}}{CF} \right]_n \quad \text{1,4 polymer}$$

A study of the reactions of 1,1,2-trifluoro-dienes with radicals and nucleophiles, and in cycloaddition reactions, was begun to extend our knowledge in this area.

The recent concern for environmental considerations prompts the environmental impact study at the end of the Experimental Section. Each chemical used is listed with its NIOSH registry number and available toxicity data. Due to the small scale and research quantitites of chemicals prepared, no detrimental effect on the environment was expected.

SECTION 2

RESULTS AND CONCLUSIONS

A study of the reactions of three 1,1,2-trifluoropentadienes has been carried out. The results of radical reactions, nucleophilic reactions, and 2 + 2 cycloadditions will be presented.

Preparation of Olefins

The three systems chosen for study were 1,1,2-trifluoropentadiene-1,3 ($CF_2{=}CFCH{=}CHCH_3$, I), 1,1,2,5,5,5-hexafluoropentadiene-1,3 ($CF_2{=}CFCH{=}CHCF_3$, II), and 1,4-perfluoropentadiene ($CF_2{=}CFCF_2CF{=}CF_2$, III). Two asymmetric centers are present in both $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ and $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ and only the trans olefins were obtained by dehydrohalogenation. For these reasons the preparations of the respective olefins, $CF_2BrCFClCH{=}CHCH_3$ and $CF_2ClCFClCH{=}CHCF_3$, and dienes $CF_2{=}CFCH{=}CHCH_3$ and $CF_2{=}CFCH{=}CHCF_3$, are treated separately. Reactions and conclusions will be discussed together to show the similarities and differences of the various dienes. Table I contains the fluorinated starting materials used in olefin preparation.

The first diene studied was 1,1,2-trifluoropentadiene-1,3 (I), which was prepared by the method of Tarrant and Gillman.[1] The following reaction scheme shows the sequence and yields of the various reactions:

TABLE I

FLUORINATED STARTING MATERIALS

Compound	Boiling Point	Preparation Method	% Yield	Infrared Figure
$CF_2BrCFClBr$	91°C	$CF_2{=}CFCl + Br_2$	90%	Figure 1
CF_2BrCF_2I	78-79°C	$CF_2{=}CF_2 + Br_2 + I_2$	28%	Figure 11
$CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ [1]	177-182°C	$CF_2BrCFClBr + CH_2{=}CHCH_3$	83%	Figures 2 and 3
$CF_2BrCF_2CH_2CH_2I$	160-161°C	$CF_2BrCF_2I + CH_2{=}CH_2$	58%	Figure 12
$CF_2Cl\overset{*}{C}FBrCF_2\overset{*}{C}FBrCF_2COONa$ [2]		$CF_2ClCFBrCF_2CFBrCF_2COF + Na_2CO_3$		
$CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3$	(56-59°C/ 0.1 mm)	$CF_2BrCFClBr + CH_2{=}CHCF_3$	25%	Figure 7
$CF_2ClCFClI$	100-101°C	$CF_2{=}CFCl + ICl$	75%	
$CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ [3]	160-161°C	$CF_2ClCFClI + CH_2{=}CHCF_3$	90%	Figure 51
CF_3NO		$CF_3CO_2NO \xrightarrow{heat} CF_3NO$		

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1) Two diastereomers. Precursor to $CF_2{=}CFCH{=}CHCH_3$ (I)
2) Two diastereomers. Precursor to $CF_2{=}CFCF_2CF{=}CF_2$ (III)
3) Two diastereomers. Precursor to $CF_2{=}CFCH{=}CHCF_3$ (II)

Reaction Scheme 1

1. $CF_2BrCFClBr + CH_2{=}CHCH_3 \xrightarrow[\text{peroxide}]{\text{autoclave}} CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$

80% yield of two diastereomers

2. $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3 \xrightarrow[\text{EtOH}]{\text{KOH}} CF_2Br\overset{*}{C}FClCH{=}CHCH_3$

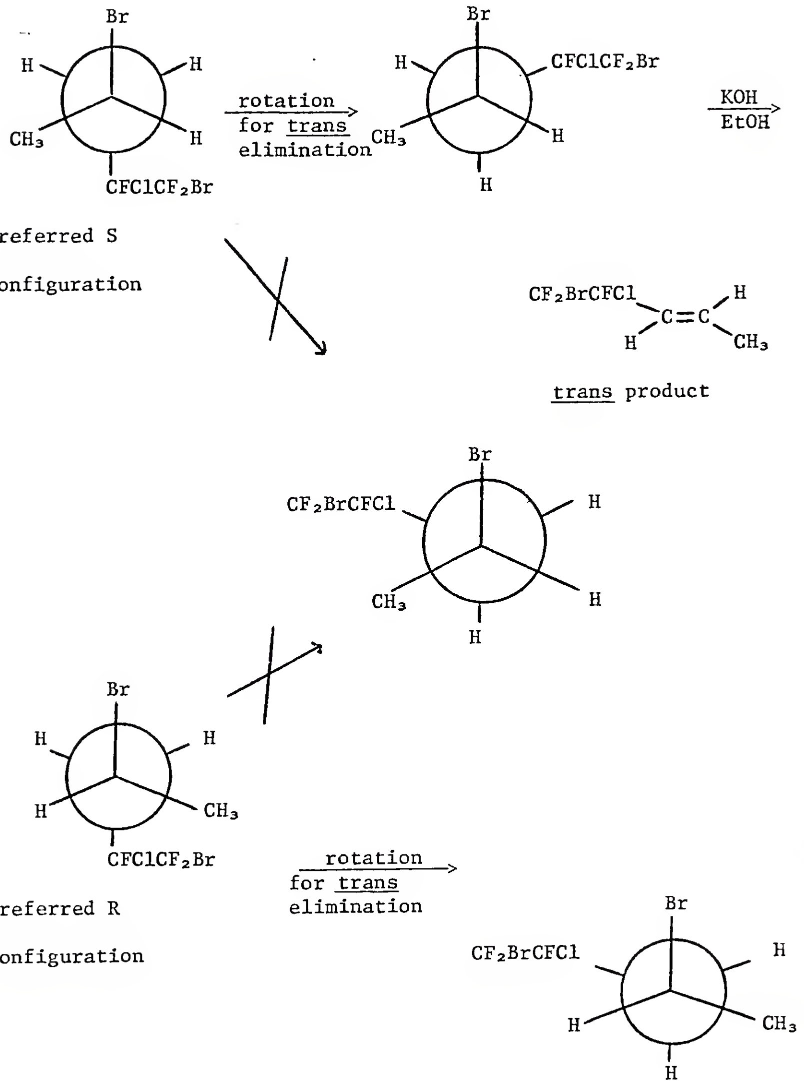
88% trans olefin only

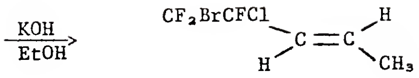
3. $CF_2Br\overset{*}{C}FClCH{=}CHCH_3 \xrightarrow[\text{EtOH}]{\text{Zinc}} CF_2{=}CFCH{=}CH_3$ 92%

Tarrant and Gillman[1] did not report the presence of two diastereomers in the products obtained in reaction 1. Their yield in step 2 was 45%. The trans geometry of $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$ obtained in step 2 was not discovered by these workers. Our procedure gave a three-fold increase in yield for the diene (I).

The two diasteromers from Step 1 were isolated on a 40-plate Oldershaw column. Each gave the same mass spectrum. However, NMR analysis indicated the components to be the two diastereomeric products.

In step 2, a reported yield of 45% was expected.[1] A much higher yield of 88% was realized from the mixed diastereomers, but the yield decreased rapidly with other impurities present. The NMR analysis also indicated only one isomer, the trans olefin, to be present. Space-filling models readily explained the exclusion of the cis olefin from the product. The presence of the chlorine and the CF_2Br group on the β carbon prohibits free rotation of the CHBr moiety. Trans elimination, being favored, gives only the trans olefin from both the R and S configuration about the asymmetric CHBr center.





The size of the $CF_2BrCFCl$ group does not allow rotation to place this group between the bromine atom and methyl group, therefore; no cis product was formed. Two possible olefins were expected from the dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$.

4. $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3 \xrightarrow[EtOH]{KOH} CF_2Br\overset{*}{C}FClCH{=}CHCH_3$

and

$CF_2BrCF{=}CH\overset{*}{C}HBrCH_3$

That the only product isolated was $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$ was attributed to the greater leaving ability of bromine compared to chlorine. In contrast, Piccardi et al.[3] reported the ethanolic potassium hydroxide dehydrohalogenation of $CF_3\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$ to give both olefins.

5. $CF_3\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3 \xrightarrow[EtOH]{KOH} CF_3CF{=}CH\overset{*}{C}HBrCH_3$

and

$CF_3\overset{*}{C}FBrCH{=}CHCH_3$

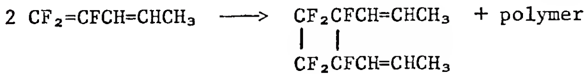
The attempted dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ using aqueous (50%) sodium hydroxide was carried out at 80°C. The two materials were immiscible and no reaction was detected over a one-hour period. Reaction of the alkane, $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$, with potassium t-butoxide in dimethyl sulfoxide gave the desired olefin, $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$, in 73% yield. Of the three reagents, ethanolic potassium hydroxide gave the best yield and purest crude product. The reaction of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ with zinc was carried out to give $CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$ as an alternate precursor to $CF_2{=}CFCH{=}CHCH_3$. The yield in this reaction, 79%, was not as good as that from $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$.

The dehalogenation in step 3 was reported to give a 60% yield with $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$. A 92% yield was realized from the pure trans olefin. The products prepared from $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ along with the preparation method, yield, and boiling points are reported in Table II. Each product was completely identified by infrared, NMR, and mass spectral analysis.

NMR and mass spectral data for each diastereomer prepared in Step 1, and each of the olefins obtained are presented in the Experimental Section. Infrared spectra are given for all starting materials as well as the reaction products.

After being stored at 0°C for 20 days, the diene had reacted to give the cyclobutane derivative and a white granular polymer.

6.



$$2\ CF_2{=}CFCH{=}CHCH_3 \longrightarrow \begin{array}{l} CF_2CFCH{=}CHCH_3 \\ |\quad\ | \\ CF_2CFCH{=}CHCH_3 \end{array} + \text{polymer}$$

TABLE II

FLUORINATED OLEFINS FROM $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$

Compound	Boiling Point	Preparation Method	% Yield	Infrared Figure
$CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$	110-111°C	$CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3 \xrightarrow[EtOH]{Zinc}$	91%	Figure 24
$CF_2Br\overset{*}{C}FClCH{=}CHCH_3$	133-134°C	$CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3 \xrightarrow[EtOH]{KOH}$	88%	Figure 13
$CF_2{=}CFCH{=}CHCH_3$	44-45°C	$CF_2Br\overset{*}{C}FClCH{=}CHCH_3 \xrightarrow[EtOH]{Zinc}$	92%	Figure 20
$CF_2CFCH{=}CHCH_3$ $CF_2CFCH{=}CHCH_3$	160-161°C	Dimerization of $CF_2{=}CFCH{=}CHCH_3$	100%	Figure 31

A higher reaction temperature is usually required for 2 + 2 cycloaddition reactions. Chlorotrifluoroethylene does not form the cyclic dimer below 175°C and even activated fluorocarbon olefins require a temperature of 100°C for extended periods of time. The remaining reactions of 1,1,2-trifluoropentadiene-1,3 were carried out on freshly prepared and distilled diene. These reactions will be reported after procedures for the preparation of the remaining dienes have been described.

To acquire information on fluorocarbon compounds which contain iodine, 1-bromo-2-iodotetrafluoroethane was prepared and added to ethylene. The butane was converted to the olefin by the following reaction scheme.

Reaction Scheme 2

1. $CF_2{=}CF_2 + Br_2 + I_2 \xrightarrow{\text{Autoclave}} CF_2BrCF_2Br\ (31\%) +$

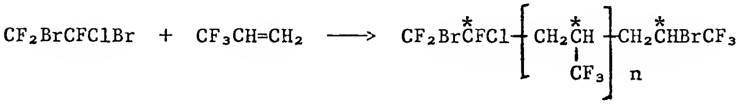
   $CF_2BrCF_2I\ (49\%) + CF_2ICF_2I\ (20\%)$

2. $CF_2BrCF_2I + CH_2{=}CH_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CF_2BrCF_2CH_2CH_2I$ 68%

3. $CF_2BrCF_2CH_2CH_2I \xrightarrow[\text{EtOH}]{\text{KOH}} CF_2BrCF_2CH{=}CH_2$ 76%

The reaction of ethylene with the iodide, CF_2BrCF_2I, was found to take place thermally at 150°C in four hours to give the desired adduct. The discovery of this fact in the preparation of the precursor for 1,1,2,5,5,5-hexafluoropentadiene-1,3 was fortuitous.

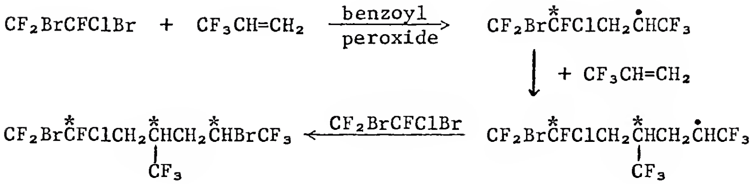
An attempt to prepare 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II) was made. The reaction of 1,2 dibromo-2-chlorotrifluoroethane with trifluoropropene was carried out using the same procedure as with propene. The only product isolated, however, was the adduct containing two moieties of trifluoropropene. This result can be attributed to the presence of the CF_3 group adjacent to the carbon containing the unpaired electron, which stabilizes this radical, $CF_2Br\overset{*}{C}FClCH_2\dot{C}HCF_3$, and makes it less reactive than $CF_2Br\overset{*}{C}FClCH_2\dot{C}HCH_3$. Tarrant and Lilyquist[2] also noted the relative inability of $CF_3CH{=}CH_2$ to form 1 to 1 adducts with $CF_2BrCFClBr$.



$$CF_2BrCFClBr + CF_3CH{=}CH_2 \longrightarrow CF_2Br\overset{*}{C}FCl\left[CH_2\underset{\underset{CF_3}{|}}{\overset{*}{C}}H\right]_n CH_2\overset{*}{C}HBrCF_3$$

n = 1, 2, 3, etc.

Higher molecular weight components were also obtained but not isolated. The following sequence for the formation of the 2 to 1 adduct is proposed.

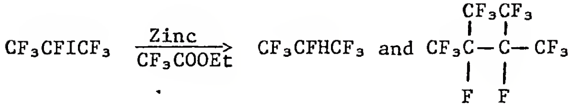


$$CF_2BrCFClBr + CF_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CF_2Br\overset{*}{C}FClCH_2\dot{C}HCF_3$$

$$\downarrow + CF_3CH{=}CH_2$$

$$CF_2Br\overset{*}{C}FClCH_2\underset{\underset{CF_3}{|}}{\overset{*}{C}}HCH_2\overset{*}{C}HBrCF_3 \xleftarrow{CF_2BrCFClBr} CF_2Br\overset{*}{C}FClCH_2\underset{\underset{CF_3}{|}}{\overset{*}{C}}HCH_2\dot{C}HCF_3$$

A diene was formed by the reaction of zinc on the octane above. It was identified by NMR, infrared analysis, and mass spectral data as $CF_2{=}CFCH_2\underset{CF_3}{\overset{*}{C}}HCH_2CH{=}CF_2$. The formation of a $CH{=}CF_2$ group with zinc was not expected since Tarrant and Keller[36] showed that coupled and reduced products predominated with fluorinated compounds containing iodine.



$$CF_3CFICF_3 \xrightarrow[CF_3COOEt]{Zinc} CF_3CFHCF_3 \text{ and } CF_3\underset{F}{\overset{CF_3}{C}}-\underset{F}{\overset{CF_3}{C}}-CF_3$$

The successful preparations of the desired 1,1,2,5,5,5-hexafluoropentadiene-1,3 was carried out following the sequence described by Tarrant and Lilyquist[2] as shown in reaction scheme 3.

Reaction Scheme 3

1. $CF_2Cl\overset{*}{C}FClI + CH_2{=}CHCF_3 \xrightarrow[\text{4 hours}]{150^\circ C} CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ 80%

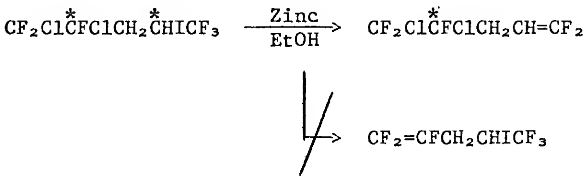
2. $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3 \xrightarrow[EtOH]{KOH} CF_2Cl\overset{*}{C}FClCH{=}CHCF_3$ 70%

   trans only

3. $CF_2Cl\overset{*}{C}FClCH{=}CHCF_3 \xrightarrow[EtOH]{Zinc} CF_2{=}CFCH{=}CHCF_3$ 80%

Two diastereomers of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ were obtained from the addition reaction, step 1. Dehydrohalogenation gave only the *trans* olefin, $CF_2Cl\overset{*}{C}FClCH{=}CHCF_3$, in step 2. Tarrant and Lilyquist[2] did not report two diastereomeric products in step 1, or the exclusive *trans* geometry for the olefin obtained in Step 2. Comparable yields were obtained by our procedures. The loss of the bulky iodine is greatly favored over the loss of chlorine and with iodine being a better leaving group, the product was exclusively the *trans* olfein. The *trans* geometry in the olefin has been previously explained for $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$ formation from $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$. The 1,1,2,5,5,5-hexafluoropentadiene-1,3, obtained in step 3, was purified on a 25-plate Oldershaw column and the correct boiling point was found to be 43-44°C instead of 50°C as reported by Tarrant and Lilyquist.[2] The sample boiling at 50°C was found to contain 92% of the desired diene and 8% of $CF_2Cl\overset{*}{C}FClCH{=}CHCF_3$.

The dehalogenation of $CF_2\overset{*}{C}lCFClCH_2\overset{*}{C}HICF_3$ with zinc in ethanol gave an interesting new olefin.



$$CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3 \xrightarrow[EtOH]{Zinc} CF_2Cl\overset{*}{C}FClCH_2CH{=}CF_2$$

$$\not\rightarrow CF_2{=}CFCH_2CHICF_3$$

The olefin was identified by the difluorovinyl absorption in the infrared (5.67μ) and F^{19} NMR data. Mass spectral analysis gave the molecular ions for the two chlorine system and a cracking pattern identifying the olefin unequivocally. The expected product, $CF_2{=}CFCH_2CHICF_3$, was not found. The list of olefins prepared from $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ is given in Table III.

The final pentadiene prepared was 1,4-perfluoropentadiene using the reaction sequence reported by Fearn et al.[30] as shown below.

Reaction Scheme 4

1. $$CF_2Cl\overset{*}{C}FBrCF_2\overset{*}{C}FBrCF_2COONa \xrightarrow{\text{heat}} CF_2Cl\overset{*}{C}FBrCF_2CF{=}CF_2 \qquad 70\%$$

2. $$CF_2Cl\overset{*}{C}FBrCF_2CF{=}CF_2 \xrightarrow[\text{EtOH}]{\text{Zinc}} CF_2{=}CFCF_2CF{=}CF_2 \qquad 75\%$$

Our synthesis gave comparable yields to that of Fearn et al.[30] Each of the compounds was identified by infrared analysis, NMR, and mass spectral data. Table IV gives the pertinent data concerning the compounds involved in the preparation of 1,4-perfluoropentadiene.

Reactions of Olefins Prepared

Cycloaddition Reactions

The 2 + 2 cycloaddition reaction of the three fluorine-containing pentadienes was studied using both fluoroolefins and fluorodienes as well as butadiene itself. Table V shows the reactions carried out in this study. The only 2 + 2 cycloaddition products isolated were from the conjugated pentadienes reacting with themselves or each other.

TABLE III

FLUORINATED OLEFIN FROM THE $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$

Compound	Boiling Point	Preparation Method	% Yield	Infrared Figure
$CF_2Cl\overset{*}{C}FClCH=CHCF_3$	88°C	$CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3 \xrightarrow[EtOH]{KOH}$	70%	Figure 55
$CF_2Cl\overset{*}{C}FClCH_2CH=CF_2$	101-103°C	$CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3 \xrightarrow[EtOH]{Zinc}$	72%	Figure 80
$CF_2=CFCH=CHCF_3$	43-44°C	$CF_2Cl\overset{*}{C}FClCH=CHCF_3 \xrightarrow[EtOH]{Zinc}$	92%	Figure 57
$CF_2CFCH=CHCF_3$ $CF_2CFCH=CHCF_3$	133-135°C	Dimerization of $CF_2=CFCH=CHCF_3$	100%	Figure 63

TABLE IV

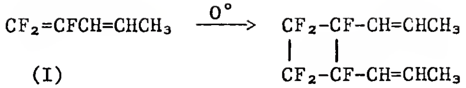
FLUORINATED OLEFINS FROM $CF_2Cl\overset{*}{C}FBrCF_2\overset{*}{C}FBrCF_2COONa$

Compound	Boiling Point	Preparation Method	% Yield	Infrared Figure
$CF_2Cl\overset{*}{C}FBrCF_2CF{=}CF_2$	104-106°C	$CF_2Cl\overset{*}{C}FBrCF_2\overset{*}{C}FBrCF_2COONa \xrightarrow{heat}$	70%	19
$CF_2{=}CFCF_2CF{=}CF_2$	36-38°C	$CF_2Cl\overset{*}{C}FBrCF_2CF{=}CF_2 \xrightarrow[EtOH]{Zinc}$	75%	29

TABLE V

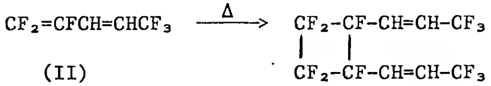
2 + 2 CYCLOADDITION REACTIONS

Olefin 1	Olefin 2	Time (Hrs)	Temp. (°C)	Product	Yield %	I.R. Figure	NMR Figure	Mass Spec. Table
$CF_2{=}CFCH{=}CHCH_3$	$CF_2{=}CFCH{=}CHCH_3$	16	100	$CF_2CFCH{=}CHCH_3$ $CF_2CFCH{=}CHCH_3$ (1)	100	31	32	XVII
$CF_2{=}CFCH{=}CHCH_3$	$CF_2{=}CCl_2$	20	160	(1)	100	31	32	XVII
$CF_2{=}CFCH{=}CHCH_3$	$CF_2{=}CFCl$	20	160	(1)	100	31	32	XVII
$CF_2{=}CFCH{=}CHCF_3$	$CF_2{=}CFCH{=}CHCF_3$	20	100	$CF_2CFCH{=}CHCF_3$ $CF_2CFCH{=}CHCF_3$ (2)	100	63	64	XXVI
$CF_2{=}CFCH{=}CHCH_3$	$CF_2{=}CFCH{=}CHCF_3$	20	105	(1), (2) plus	30 (1)	65	76	XXVII
				$CF_2CFCH{=}CHCH_3$	45 (3)			
				$CF_2CFCH{=}CHCF_3$	20 (2)			
$CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$	$CF_2{=}CFCl$	20	140	No cyclo-addition products formed				
$CF_2{=}CFCF_2CF{=}CF_2$	$CF_2{=}CFCF_2CF{=}CF_2$	20	140	No cyclo addition products formed				
$CF_2{=}CFCH{=}CHCH_3$	$CH_2{=}CHCH{=}CH_2$	4	120	(1)	100	31	32	XVII
$CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$	$CH_2{=}CHCH{=}CH_2$	20	125	No cyclo-addition products formed				
$CF_2{=}CFCF_2CF{=}CF_2$	$CF_2{=}CFCl$	48	160	No cyclo-addition products formed				



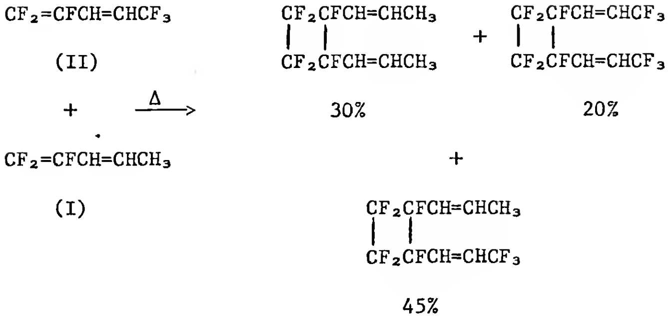
$$\mathrm{CF_2{=}CFCH{=}CHCH_3} \xrightarrow{0^\circ} \begin{array}{l} \mathrm{CF_2{-}CF{-}CH{=}CHCH_3} \\ |\qquad | \\ \mathrm{CF_2{-}CF{-}CH{=}CHCH_3} \end{array}$$

(I)



$$\mathrm{CF_2{=}CFCH{=}CHCF_3} \xrightarrow{\Delta} \begin{array}{l} \mathrm{CF_2{-}CF{-}CH{=}CH{-}CF_3} \\ |\qquad | \\ \mathrm{CF_2{-}CF{-}CH{=}CH{-}CF_3} \end{array}$$

(II)



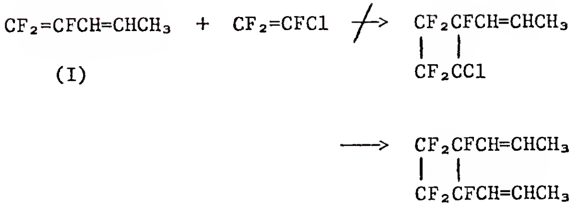
$$\begin{array}{c} \mathrm{CF_2{=}CFCH{=}CHCF_3} \\ (II) \\ + \\ \mathrm{CF_2{=}CFCH{=}CHCH_3} \\ (I) \end{array} \xrightarrow{\Delta} \begin{array}{l} \mathrm{CF_2CFCH{=}CHCH_3} \\ |\quad | \\ \mathrm{CF_2CFCH{=}CHCH_3} \end{array} + \begin{array}{l} \mathrm{CF_2CFCH{=}CHCF_3} \\ |\quad | \\ \mathrm{CF_2CFCH{=}CHCF_3} \end{array} + \begin{array}{l} \mathrm{CF_2CFCH{=}CHCH_3} \\ |\quad | \\ \mathrm{CF_2CFCH{=}CHCF_3} \end{array}$$

30% 20% 45%

The mixed cyclobutane was observed along with the two expected homocyclobutane products when a mixture of the 1,1,2-trifluoropentadiene-1,3 and 1,1,2,5,5,5-hexafluoropentadiene-1,3 was allowed to react.

The relative amounts of the cyclobutane products are almost a statistical distribution suggesting the two dienes have the same order of reactivity.

The attempted reaction of other olefins, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, and $CH_2{=}CHCH{=}CH_2$ with the 1,1,2-trifluoro-dienes resulted in cyclobutane products containing only the 1,1,2-trifluoro-diene molecules.



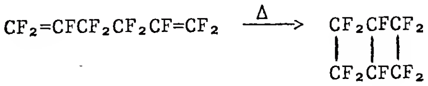
$$CF_2{=}CFCH{=}CHCH_3 + CF_2{=}CFCl \not\longrightarrow \begin{array}{l} CF_2CFCH{=}CHCH_3 \\ |\quad\ | \\ CF_2CCl \end{array}$$

(I)

$$\longrightarrow \begin{array}{l} CF_2CFCH{=}CHCH_3 \\ |\quad\ | \\ CF_2CFCH{=}CHCH_3 \end{array}$$

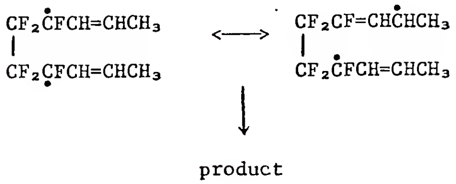
We conclude that the reactivity of the 1,1,2-trifluoro-dienes in forming 2 + 2 cyclobutane products is much greater than fluorinated olefins such as $CF_2{=}CFCl$.

Fluorocarbon dienes react to give cyclobutane products both intra and intermolecularly. The thermal reaction of perfluorohexadiene-1,5 has been reported to give the intramolecular 2 + 2 cycloaddition product.[37]



$$CF_2{=}CFCF_2CF_2CF{=}CF_2 \xrightarrow{\Delta} \begin{array}{l} CF_2CFCF_2 \\ |\quad\ |\quad | \\ CF_2CFCF_2 \end{array}$$

In general the reaction conditions for 2 + 2 cycloaddition reactions are rather harsh, i.e, temperatures exceeding 200°C for the cycloaddition reaction to predominate. The substituent effect is noteworthy since ethers, $CF_2{=}CFOR$, react more readily than vinyl alkanes or perfluorinated olefins in the preparation of cyclobutane products. The formation of a cyclobutane product from $CF_2{=}CFCH{=}CHCH_3$ (I) at 0°C was totally unexpected. Literature accounts gave no indication of any olefins undergoing a 2 + 2 cycloaddition at such mild conditions. The stabilization of the proposed biradical intermediate coupled with the conjugated system is credited with this result.



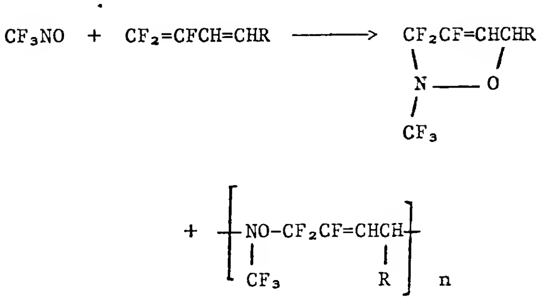
In none of the reactions was any cyclohexene products isolated thus indicating that no 2 + 4 Diels-Alder addition had occurred. The conjugated fluorinated pentadiene systems react preferentially to give 2 + 2 cycloaddition products.

The activation of the trifluorovinyl moiety by conjugation of a hydrocarbon olefin is very evident in the 2 + 2 cycloaddition reactions. Note should be taken of the decreased reactivity of $CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$ as compared to that of both $CF_2{=}CFCH{=}CHCH_3$ and $CF_2{=}CFCH{=}CHCF_3$. 1,4-Perfluoropentadiene, moreover, showed no activity towards this type of reaction as none of the cyclobutane product was found.

Radical Additions

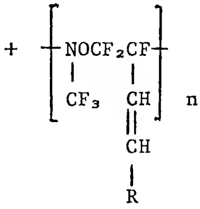
A study was made of the reaction of the three dienes with trifluoronitrosomethane (CF_3NO), with bromine (Br_2), and with bromotrichloromethane (CCl_3Br) in the presence of benzoyl peroxide.

Trifluoronitrosomethane is reported to react with fluorinated olefins by a radical anion mechanism.[22] Both partially fluorinated dienes, 1,1,2-trifluoropentadiene-1,3 (I) and 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II) gave 2 + 4 Diels-Alder type products with CF_3NO as well as polymers in which 1,2 and 1,4 addition structures were observed. The polymer was isolated and analyzed by infrared analysis. The spectrum showed absorptions at 5.65μ and 5.82μ, indicative of both 1,2 and 1,4 structures.



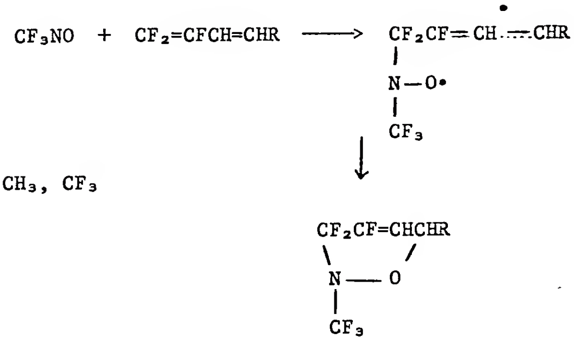
The 1,4 polymer structure

R = CH_3, CF_3



The 1,2 polymer structure

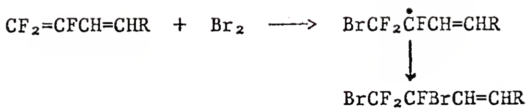
The Diels-Alder products obtained from the reaction of trifluoronitrosomethane with I and II were not unexpected since hexafluorobutadiene-1,3 gives the 2 + 4 cycloaddition product from the reaction with trifluoronitrosomethane.[13] Stabilization of the intermediate radical anion by resonance would explain the 2 + 4 cycloaddition result.



$R = CH_3, CF_3$

The 1,4-perfluoropentadiene did not react with CF_3NO either at -78°C or room temperature.

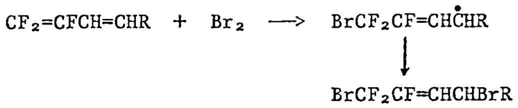
We consider halogen addition to be a radical process for fluorine-containing dienes. Two of the three dienes do contain hydrocarbon segments and we would expect addition to the hydrocarbon segment if the halogen addition were an electrophilic process. The actual product obtained was formed by addition to the CF_2=CF moiety. The process is described by the following sequence.



$$\begin{array}{l} CF_2{=}CFCH{=}CHR + Br_2 \longrightarrow BrCF_2\dot{C}FCH{=}CHR \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad BrCF_2CFBrCH{=}CHR \end{array}$$

R = CH_3, CF_3

1,2 addition product



$$\begin{array}{l} CF_2{=}CFCH{=}CHR + Br_2 \longrightarrow BrCF_2CF{=}CH\dot{C}HR \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad BrCF_2CF{=}CHCHBrR \end{array}$$

1,4 addition product

The 1,1,2,5,5,5-hexafluoropentadiene-1,3 gave both addition products with bromine while 1,1,2-trifluoropentadiene-1,3 gave only the 1,2 addition product. If the addition had been electrophilic in nature, the 1,1,2-trifluoropentadiene-1,3 would have been expected to yield the 1,4-addition product. These results are in accord with the findings of Rondarev et al.[25] who report the addition of iodine monochloride to $CF_2{=}CFCH{=}CHCF_3$, a fluorine-containing 1,3-pentadiene, gave the 1,4 addition product, while P. Brown et al.[38] found halogen addition to 5,5,5-trifluoropentadiene-1,3 to give both 1,2 and 1,4 addition.

$CF_3CH{=}CHCH{=}CH_2 + Br_2 \longrightarrow CF_3CHBrCH{=}CHCH_2Br$ 1,4 addition

$CF_3CH{=}CHCHBrCH_2Br$ 1,2 addition

1,4-Perfluoropentadiene gave 1,2 bromine addition with no tetrabromo addition product or cyclization products being formed. Bromotrichloromethane was added to 1,1,2-trifluoropentadiene-1,3

(I) and 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II), using benzoyl peroxide as the initiator. The 1,1,2-trifluoropentadiene-1,3 gave the 1,2-addition product while the 1,1,2,5,5,5-hexafluoropentadiene-1,3 gave higher telomers but none of the one to one adduct.

$$CCl_3Br + CF_2{=}CFCH{=}CHCH_3 \longrightarrow CCl_3CF_2\overset{*}{C}FBrCH{=}CHCH_3$$

$$CCl_3Br + CF_2{=}CFCH{=}CHCF_3 \longrightarrow \text{higher telomers}$$

The resonance stabilization of the intermediate radical and subsequent addition of another olefinic molecule has already been noted above. The addition of CCl_3Br was also carried out with $CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$ to give two diastereomers of $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$. A reaction was attempted between 2-iodoheptafluoropropane and 1,4-perfluoropentadiene at 150°C for 36 hours. No addition product formed and the starting materials were recovered.

Table VI gives the products from the reactions of CF_3NO, CCl_3Br, and Br_2 with the dienes.

Reactions with Nucleophiles

The reaction of nucleophiles with fluorine-containing olefins is well documented in the literature. The study of nucleophilic attack of dienes, however, has been limited to hexafluorobutadiene-1,3. The addition of Grignard reagents to perfluorinated olefins normally gives substitution products by a SN_2' type of reaction.

TABLE VI

RADICAL ADDITION REACTIONS

Olefin	Radical Source	Time (hr)	Temp (°C)	Products	Yield (%)	I.R. Fig.	NMR Fig.	Mass Spec. Table	Initiator
$CF_2{=}CFCH{=}CHCH_3$	CCl_3Br	4	70	$CF_2CFCH{=}CHCH_3$ (1) $CF_2CFCH{=}CHCH_3$ and	60 (1)				Benzoyl Peroxide
				$CCl_3CF_2\overset{*}{C}FBrCH{=}CHCH_3$ (2)	40 (2)	60	61	XXV	
$CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$	CCl_3Br	16	160	Two diastereomers of $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$	65	34	35	XVIII	Benzoyl Peroxide
$CF_2{=}CFCH{=}CHCF_3$	CCl_3Br	20	80	No 1/1 adduct or polymers					Benzoyl Peroxide
$CF_2{=}CFCF_2CF{=}CF_2$	CF_3CFICF_3	36	155	No 1/1 products or polymers					Heat
$CF_2{=}CFCF_2CF{=}CF_2$	CF_3NO	48	0	No 1/1 adduct or polymers					
		48	-78						
$CF_2{=}CFCH{=}CHCH_3$	CF_3NO	48	-78	$CF_2CF{=}CHCHCH_3$ N O CF_3 (3) + 1,2 and 1,4 polymers	50 (3)	57	48	XXI	
$CF_2{=}CFCH{=}CHCF_3$	CF_3NO	24	-78	$CF_2CF{=}CHCHCF_3$ N O + 1, 2 and CF_3 1,4 polymers	50 (4) 30 (polymer)	72	74	XXIX	

TABLE VI (Continued)

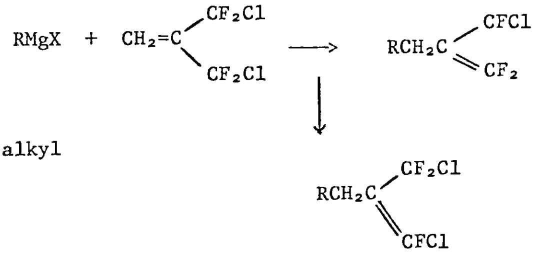
Olefin	Radical Source	Time (hr)	Temp (°C)	Products	Yield (%).	I.R. Fig.	NMR Fig.	Mass Spec. Table
$CF_2=CFCF_2CF=CF_2$	Br_2	1	50	$CF_2Br\overset{*}{C}FBrCF_2CF=CF_2$	76	38	39	
$CF_2=CFCH=CHCH_3$	Br_2	1	3	$CF_2Br\overset{*}{C}FBrCH=CHCH_3$	95	45	46	XV
$CF_2=CFCH=CHCF_3$	Br_2	1	0	$CF_2Br\overset{*}{C}FBrCH=CHCH_3$ (25%) and $CF_2BrCF=CH\overset{*}{C}HBrCF_3$ (75%)	96	70	71	XXVIII

$$RMgX + CF_2{=}CFR' \longrightarrow RCF{=}CFR' + MgFX$$

Aromatic Grignard reagents give predominant products containing conjugated double bonds.[32]

$$C_6H_5MgBr + CF_2{=}CFCF_2Cl \longrightarrow \begin{array}{ll} C_6H_5CF{=}CFCF_2Cl & 32\% \\ + & \\ C_6H_5CF_2CF{=}CF_2 & 8.6\% \end{array}$$

Alkyl Grignard reagents react with fluorohaloolefins to give an alkene in which the more easily eliminated halogen anion is displaced.



predominant product

R = alkyl

A good review of the reaction of Grignard reagents, both alkyl and aryl, can be found in <u>Chemistry of Organic Fluorine Compounds</u> by M. Hudlicky.[18]

Alkyl Grignard reagents undergo either addition-elimination or alkyl addition by radical means. The alkyl addition reaction was well documented by K. Okuhara[14] for fluoroolefins.

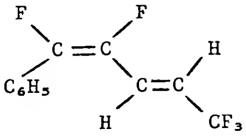
$$\mathrm{RMgX} + \mathrm{CF_2{=}CCl_2} \longrightarrow \mathrm{RCF_2CCl_2H} + \mathrm{RCF{=}CCl_2}$$

R = alkyl predominant product

The alkyl addition product was found to be formed by a radical process and not hydrolysis of the magnesium complex, $\mathrm{RCF_2CCl_2MgBr}$.

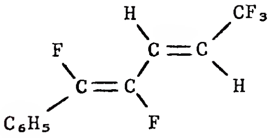
The reaction of phenylmagnesium bromide with each of the dienes gave the expected addition-elimination reaction products. The 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II) was characterized by a good yield (68%) of both cis,trans and trans,trans dienes.

$\mathrm{CF_2{=}CFCH{=}CHCF_3} + \mathrm{C_6H_5MgBr} \longrightarrow$



cis,trans

and



trans,trans

When the reaction was run at -30°C and quenched with D_2O instead of water, the only product isolated was the substituted derived diene. This result suggests a concerted reaction since no deuterium was incorporated into the product.

The product contained only the diene conjugated with the benzene ring. Since the nonconjugated product was a possibility, the stabilization of the conjugated product was the predominated factor in determining the course of the reaction.

$$\begin{tikzcd} C_6H_5MgBr \;+\; CF_2{=}CFCH{=}CHCF_3 \arrow[r] \arrow[dr, "\times" marking] & C_6H_5CF{=}CFCH{=}CHCF_3 \\ & C_6H_5CF_2CF{=}CHCH{=}CF_2 \end{tikzcd}$$

The proposed mechanism for nucleophilic addition can be shown as follows.

$$\begin{tikzcd} R^{\ominus} \;+\; CF_2{=}CFCH{=}CHR' \arrow[r] & RCF_2\overset{\ominus}{C}FCH{=}CHR' \arrow[r] & 1,\ 2,\ 3 \\ & RCF_2CF{=}CH\overset{\ominus}{C}HR' & \end{tikzcd}$$

$R' = CH_3,\ CF_3$

$R = CH_3CH_2O^{\ominus},\ C_6H_5^{\ominus}$

1. $RCF{=}CFCH{=}CHR'$ addition-elimination or substitution
2. $RCF_2CFHCH{=}CHR'$ 1,2-addition
3. $RCF_2CF{=}CHCH_2R'$ 1,4-addition

Table VII show the nucleophilic reactions with the fluorinated 1,1,2-trifluoro-diene systems. The addition of ethanolic potassium hydroxide to 1,1,2-trifluoropentadiene-1,3 and 1,1,2,5,5,5-hexafluoropentadiene-1,3 gave both 1,2 and 1,4 addition products for the trifluoropentadiene system and only 1,4 addition product for the more fluorinated hexafluoropentadiene system.

$$CF_2{=}CFCH{=}CHCH_3 + CH_3CH_2OH \xrightarrow{KOH} CH_3CH_2OCF_2CFHCH{=}CHCH_3$$

1,2 addition product

and

$CH_3CH_2OCF_2CF{=}CHCH_2CH_3$

1,4 addition product

$$CF_2{=}CFCH{=}CHCF_3 + CH_3CH_2OH \xrightarrow{KOH} CH_3CH_2OCF_2CF{=}CHCH_2CF_3$$

1,4 addition product only

The stabilization of the proposed anion intermediate by the CF_3 moiety of 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II) as compared to the CH_3 group of 1,1,2-trifluoropentadiene-1,3 (I) would explain the predominance of the 1,4 addition product in the more fluorinated system. Each adduct was unstable in moist air and hydrolyzed to an acid fluoride.

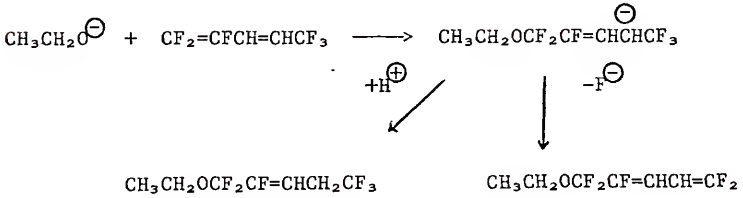
Since the nucleophilic attack of ethanolic potassium hydroxide on 1,1,2,5,5,5-hexafluoropentadiene-1,3 gave only the 1,4-addition

TABLE VII

NUCLEOPHILIC REACTIONS

Nucleophiles	Olefin	Time (Hrs)	Temp. (°C)	Product	Yield %	I.R. Figure	NMR Figure
$CH_3CH_2O^{\ominus}/CH_3CH_2OH$	$CF_2{=}CFCH{=}CHCH_3$	1	35	$CH_3CH_2OCF_2\overset{*}{C}FHCH{=}CHCH_3$ (80%)	65	42	43
				$CH_3CH_2OCF_2CF{=}CHCH_2CH_3$ (20%)			
$CH_3CH_2O^{\ominus}/CH_3CH_2OH$	$CF_2{=}CFCH{=}CHCF_3$	1	56	$CH_3CH_2OCF_2CF{=}CHCH_2CF_3$	67	67	68
$C_6H_5^{\ominus}MgBr^{\oplus}$	$CF_2{=}CFCH{=}CHCH_3$	5	37	$C_6H_5CF{=}CFCH{=}CHCH_3$	15	76	
$C_6H_5^{\ominus}\ MgBr^{\oplus}$	$CF_2{=}CFCH{=}CHCF_3$	1	50	Both Cis and Trans Isomers $C_6H_5CF{=}CFCH{=}CHCF_3$	68	77	78

product, the possibility of an attack of the first carbon followed by elimination of fluoride at the five carbon was possible.

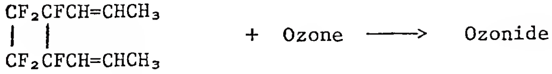


$$CH_3CH_2O^{\ominus} + CF_2{=}CFCH{=}CHCF_3 \longrightarrow CH_3CH_2OCF_2CF{=}CH\overset{\ominus}{C}HCF_3$$

$$\xrightarrow{+H^{\oplus}} CH_3CH_2OCF_2CF{=}CHCH_2CF_3 \qquad \xrightarrow{-F^{\ominus}} CH_3CH_2OCF_2CF{=}CHCH{=}CF_2$$

None of this diene was detected. The low reactivity of 1,1,2-trifluoropentadiene-1,3 toward aryl Grignard reagents could not readily be explained since nucleophilic attack of ethoxide gave essentially the same yield as the more fluorinated pentadiene, 1,1,2,5,5,5-hexafluoropentadiene-1,3.

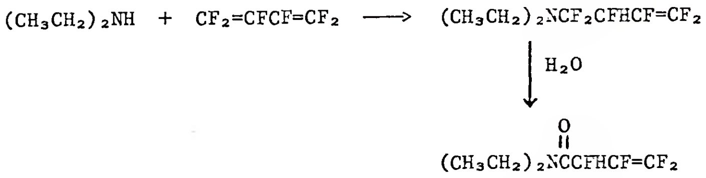
Several miscellaneous reactions were carried out on products as well as on the pentadienes. The cyclic dimer of $CF_2{=}CFCH{=}CHCH_3$ was treated with ozone in methylene chloride until no starting olefin remained.



$$\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ |\quad\; | \\ CF_2CFCH{=}CHCH_3 \end{array} + \text{Ozone} \longrightarrow \text{Ozonide}$$

The viscous product showed reactivity with potassium iodide indicating the presence of the ozonide. An attempt to decompose the ozonide gave polymeric tars.

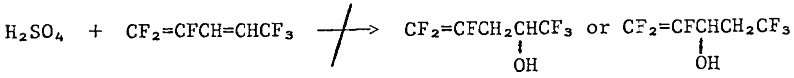
Since Knunyants et al.[20] found reaction of diethyl amine with hexafluorobutadiene-1,3 to give the addition product, the reaction with 1,1,2-trifluoropentadiene-1,3 was expected to give the addition product.



$$(CH_3CH_2)_2NH + CF_2{=}CFCF{=}CF_2 \longrightarrow (CH_3CH_2)_2NCF_2CFHCF{=}CF_2 \xrightarrow{H_2O} (CH_3CH_2)_2N\overset{O}{\overset{\|}{C}}CFHCF{=}CF_2$$

Hydrolysis gave the N,N-diethylamide as shown. The attempted reaction of diethylamine with the 1,1,2-trifluoropentadiene-1,3 gave no adduct after 48 hours. The 2 + 2 cyclodimer was the only isolated product.

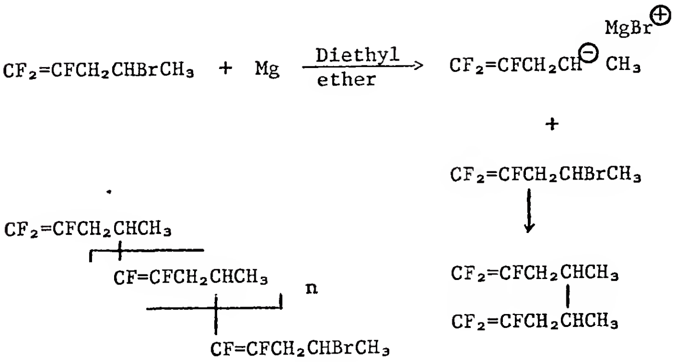
No reaction was observed after six hours when 1,1,2,5,5,5-hexafluoropentadiene-1,3 was treated with 20% sulfuric acid. The electrophilic addition to the hydrocarbon segment of the diene was expected.



$$H_2SO_4 + CF_2{=}CFCH{=}CHCF_3 \not\longrightarrow CF_2{=}CFCH_2\underset{OH}{\underset{|}{C}}HCF_3 \text{ or } CF_2{=}CF\underset{OH}{\underset{|}{C}}HCH_2CF_3$$

Apparently, both the $CF_2{=}CF$ and CF_3 groups destabilize the carbonium ion which would be formed in the first step of the reaction.

One of the intermediate olefins, $CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$, was treated with magnesium in diethyl ether to give a 10% yield of the desired coupled product along with polymeric material. The proposed scheme is as follows.



The polymer was not characterized fully since the yield was low and most of the recovered material was tar.

Conclusions

The activation of the trifluorovinyl segment of the 1,1,2-trifluoropentadiene-1,3 (I) by the hydrocarbon unsaturated segment was immediately evident in the 2 + 2 cycloaddition reaction. There has been no previous report of a cyclobutane formed at 0°C from a fluorinated olefin or diene. The 1,1,2-trifluoropentadiene-1,3 was so reactive that no other 2 + 2 cycloaddition products were formed with a variety of olefins, both fluorocarbon and hydrocarbon. Radical reactions such as bromine addition and bromotrichloromethane addition gave the 1,2 addition product, while the trifluoronitrosomethane gave the 2 + 4 Diels-Alder adduct along with polymer containing 1,2 and 1,4 addition structure.

Nucleophilic additions to 1,1,2-trifluoropentadiene-1,3 gave the expected results for aryl Grignard reagents and both 1,2 and 1,4 addition for the reaction with ethoxide.

Reactions with the 1,1,2,5,5,5-hexafluoropentadiene-1,3 (II) also show the reactivity of the mixed trifluorovinyl, hydrocarbon olefin combination. This diene readily formed the expected cyclobutane derivative. A mixed cyclobutane was found when 1,1,2-trifluoropentadiene-1,3 was treated with (II). Bromine added 1,2 and 1,4 to give the corresponding alkenes in 25% and 75% yields, respectively. The reaction of bromotrichloromethane gave only polymers with 1,1,2,5,5,5-hexafluoropentadiene-1,3. Trifluoronitrosomethane again gave the 2 + 4 Diels-Alder adduct with (II) along with polymers with 1,2 and 1,4 structures. The expected elimination or substitution reaction from aryl Grignard reagents was realized in 68% yield, giving both the cis,trans and trans,trans products. Ethanol addition gave only the 1,4 addition product in 67% yield.

The 1,4-perfluoropentadiene was found to be unreactive compared to (I) and (II). No 2 + 2 cycloaddition products were formed and no products from radical reactions were isolated except for the 1,2 addition product with bromine. None of the tetrabromo addition product or cyclized product was formed. Trifluoronitrosomethane gave no adducts at -78°C and at ambient temperature.

Tables VIII, IX and X give the reactions, products, and yields for each system, 1,1,2-trifluoropentadiene-1,3; 1,1,2,5,5,5-hexafluoropentadiene-1,3; and 1,4-perfluoropentadiene.

TABLE VIII

REACTIONS OF THE 1,1,2-TRIFLUOROPENTADIENE-1,3

Reaction Type	Reactant	Time (hr)	Temp (°C)	Products	Yield (%)	Comments
2 + 2 Cycloaddition	$CF_2{=}CFCl$	20	160	$\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ \vert \quad \vert \\ CF_2CFCH{=}CHCH_3 \end{array}$	100	No adduct formed between CTFE and 1,1,2-trifluoropentadiene-1,3
2 + 2 Cycloaddition	$CF_2{=}CCl_2$	16	160	$\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ \vert \quad \vert \\ CF_2CFCH{=}CHCH_3 \end{array}$	100	
2 + 2 Cycloaddition	$CF_2{=}CFCH{=}CHCH_3$	16	100	$\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ \vert \quad \vert \\ CF_2CFCH{=}CHCH_3 \end{array}$	100	
2 + 2 Cycloaddition	$CF_2{=}CFCH{=}CHCF_3$	20	105	$\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ \vert \quad \vert \\ CF_2CFCH{=}CHCF_3 \end{array}$	45	The yield of homodimers (cyclic) was 55%
2 + 2 Cycloaddition	$CH_2{=}CHCH{=}CH_2$	4	120	None of the hydrocarbon product		No reaction
Radical	CCl_3Br	4	70	$CCl_3CF_2\overset{*}{C}FBrCH{=}CHCH_3$	40	Only the 1,2 addition product
				+ 2+2 Cycloaddition product	60	

TABLE VIII (Continued)

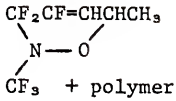
Radical	CF_3NO	48	-78	2+4 Diels-Alder Product polymer 1,2 and 1,4	50 50	 + polymers
Radical	Br_2	30	3	$CF_2BrCFBrCH=CHCH_3$	95	Only the 1,2 addition product
Nucleophilic	$CH_5CH_2O^{\ominus}H^{\oplus}$	1	35	$CH_3CH_2OCF_2CFHCH=CHCH_3$ (80%) $CH_3CH_2OCF_2CF=CHCH_2CH_3$ (20%)	65	Both 1,2 and 1,4 addition products formed
Nucleophilic	C_6H_5MgBr	5	37	$C_6H_5CF=CF=CHCH_3$	15	Slow reaction, lower yield.

TABLE IX

REACTIONS OF THE 1,1,2,5,5,5-HEXAFLUOROPENTADIENE-1,3

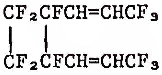
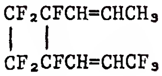
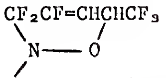
Reaction Type	Reactant	Time (Hr)	Temp. (°C)	Product	Yield (%)	Comments
2 + 2 Cycloaddition	$CF_2{=}CFCH{=}CHCF_3$	20	100	 $\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ \vert\quad\ \vert \\ CF_2CFCH{=}CHCF_3 \end{array}$	100	Quantitative yield of the cyclobutane dimer
2 + 2 Cycloaddition	$CF_2{=}CFCH{=}CHCH_3$	20	105	 $\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ \vert\quad\ \vert \\ CF_2CFCH{=}CHCF_3 \end{array}$	45	
Radical	CCl_3Br	20	80	Polymers		No 1/1 adduct
Radical	CF_3NO	24	-78	2 + 4 Diels-Alder adduct and both 1,2 and 1,4 polymer	50	 $CF_2CF{=}CHCHCF_3$, N—O, CF_3 + polymers
Radical	Br_2	1	0	$CF_2Br\overset{*}{C}FBrCH{=}CHCF_3$ (25%) $CF_2BrCF{=}CH\overset{*}{C}HBrCF_3$ (75%)	96	Both 1,2 and 1,4 adducts formed
Nucleophilic	$CH_3CH_2\overset{\ominus}{O}\overset{\oplus}{H}$	1	56	$CH_3CH_2OCF_2CF{=}CHCH_2CH_3$	67	Only the 1,4 adduct formed
Nucleophilic	C_6H_5MgBr	1	50	$C_6H_5CF{=}CFCH{=}CHCF_3$	68	Both cis,trans and trans,trans isomers formed

TABLE X

REACTIONS OF THE PERFLUOROPENTADIENE-1,4

Reaction Type	Reactants	Time (hr)	Temp. (°C)	Products	Yield (%)
Cycloaddition	$CF_2=CFCF_2CF=CF_2$	20	140	No cycloaddition product	
Cycloaddition	$CF_2=CFCl$	48	160	No cycloaddition product	
Radical	CF_3CFICF_3	36	155	No radical addition	
Radical	CF_3NO	48	-78	No radical addition	
		48	0		
Radical	Br_2	1	50	$CF_2BrCFBrCF_2CF=CF_2$	76

SECTION 3

EXPERIMENTAL

The analytical work on the compounds prepared was carried out as follows: Gas-liquid chromatography (GLC) was accomplished on a Hewlett Packard 5710A gas chromatograph equipped with a thermal conductivity detector. A 20-foot QF-1 column with a 10% loading on acid washed Chromosorb W was the column of choice. A methyl trifluoropropyl silicone oil (QF-1) proved adequate for separation of the fluorine-containing products. Infrared analyses were performed using a liquid smear of sample between sodium chloride crystals. A Perkin Elmer 727B instrument was employed. Nuclear magnetic resonance (NMR), both proton H^1 and fluorine F^{19}, were performed by Dr. Wallace Brey using a Varian XL-100 spectrometer with external standard. Mass spectral data were compiled on an AEI-MS-30 mass spectrometer with a DS-30 data system with the assistance of Dr. Roy King and Ms. Jackie Dugan. Any deviation, such as column change for GLC analysis, etc., will be presented in the experimental for specific reactions. All temperatures are reported in degrees centigrade (C) with boiling points being as observed and uncorrected.

Preparation of Precursors

Addition of 1,2-Dibromo-2-chlorotrifluoroethane ($CF_2BrCFClBr$) to Propene ($CH_2=CHCH_3$)

The attempted reaction was carried out in a five-liter, three-necked flask equipped with a gas inlet, a condenser, a thermowell, and backed by a Dry-Ice acetone trap. The 1,2-dibromo-2-chlorotrifluoroethane (CTFE dibromide, 1,385 grams, 5 moles) was added and stirred under a dry nitrogen sweep for two hours while the material was heated to reflux. Benzoyl peroxide (10 grams) was added and the propene ($CH_2=CHCH_3$) addition was begun. After one hour, an additional five grams of benzoyl peroxide was added and, subsequently, five grams every hour for three additional hours. At the end of four hours, a sample revealed no addition product had formed even though there had been added 170 grams (4 moles) of propene. The reaction was terminated and the starting materials recovered (Figure 1).

A three-liter autoclave was cleaned, equipped with a 5,000 psi rupture disc and pressure checked with dry nitrogen. The autoclave was evacuated and cooled in liquid oxygen before a mixture of CTFE dibromide ($CF_2BrCFClBr$, 1,385 grams, 5 moles) and benzoyl peroxide (20 grams) was added. The propene ($CH_2=CHCH_3$, 210 grams, 5 moles) was condensed into the autoclave through a vacuum manifold. After the system was warmed to ambient temperature, the autoclave was placed in a heater/rocker and heated to 150°C with rocking for 16 hours. The autoclave was cooled to room temperature and the overgases collected. The remaining liquid (1,505 grams) was distilled to give 880 grams of starting $CF_2BrCFClBr$ along with 485 grams of material which had a boiling point of 176-181°C (83% yield). A GLC analysis on an SE-30 nickel column showed two components which did not give a base line separation. Further separation was carried out on a 40-plate Oldershaw column to give the two fractions in greater than 90% purity. Nuclear magnetic resonance analysis confirmed the structure to be two diastereomers of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (Figures 2 - 6). Figure 2 - lower boiling diastereomer. IR (liquid) maxima in microns 3.34 (C-H), 8.1, 8.18, 8.32, 8.95 (C-F), 9.6, 10.0, 10.4, 12.55. Figure 3 - higher boiling diastereomer. IR (liquid) maxima in microns 3.3 (C-H), 8.1, 8.15, 8.33 (C-F), 9.5, 12.5, 12.7. Figure 4 - F^{19} NMR, two fluorines, doublet for CF_2Br; one fluorine, multiplet for CFCl; mass spectrum m/e 320 (M^+), 239, 237 (M-Br), 203, 201 (M-Br and Cl), 159, 157 (M-2Br), 121 ($M-C_2F_3ClBr$). High resolution mass spectrum, $C_5F_3Br_2ClH_6$, calculated mass 315.84, measured 315.85.

The three-liter autoclave reaction was repeated to obtain an additional 472 grams (80% yield) of material, $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$, for further reactions.

A three-liter autoclave reaction was repeated using propene (210 grams, 5 moles), 1,2-dibromo-2-chlorotrifluoroethane (2,806 grams, 10.2 moles) and benzoyl peroxide (30 grams). The reaction was carried out at 150°C for 24 hours and was worked up as the previous reactions. The liquid products were distilled to give 661 grams of the two diastereomers in 80% yield based on consumed propene.

Attempted Reaction of 1,2-Dibromo-2-chlorotrifluoroethane ($CF_2BrCFClBr$) with 1,3-Butadiene ($CH_2=CHCH=CH_2$)

A three-liter autoclave was cleaned and equipped with a 5,000 psi rupture disc before being pressure checked with 600 psi of dry nitrogen. After venting the nitrogen, a full vacuum was applied and the autoclave was cooled to -196°C with liquid oxygen. Benzoyl peroxide (15 grams) was dissolved in the 1,2-dibromo-2-chloro-trifluoroethane (1,040 grams) and sucked into the evacuated autoclave. The 1,3-butadiene (135 grams) was vacuum transferred into the autoclave and the system was heated to 120°C for 16 hours. After the autoclave was cooled to ambient temperature, the overgases were collected (120 grams). Distillation gave recovered 1,2-dibromo-2-chlorotrifluoroethane (996 grams) and ∿30 grams of higher molecular weight oil. The simple adduct (1 to 1) was not present.

Addition of 1,2-Dibromo-2-chlorotrifluoroethane ($CF_2BrCFClBr$) to Trifluoropropene ($CF_3CH=CH_2$)

A three-liter autoclave was equipped with a 5,000 psi rupture disc and pressure checked to 700 psi with dry nitrogen. The nitrogen was vented and a full vacuum applied to the system before the autoclave was cooled to -196°C with liquid oxygen. The 1,2-dibromo-2-chloro-trifluoroethane (1,108 grams) in which benzoyl peroxide (15 grams) was dissolved was then sucked into the evacuated autoclave. Trifluoropropene (266 grams) was condensed into the system before the autoclave was heated to 120°C and rocked for 20 hours. After the system was cooled to room temperature, the overgases were collected (101 grams) and the liquid products poured into a distillation flask. The

1,2-dibromo-2-chlorotrifluoroethane was recovered (960 grams) leaving 280 grams of higher boiling material. Distillation gave 105 grams of material with a boiling point less than 180°C which by GLC analysis was a composite of four peaks. The higher boiling fraction (90 grams, bp 56-59°/0.1 mm) was found to be two sets of diastereomers of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3$ (25% yield, Figures 7 - 10). Figure 7 - IR (liquid) maxima in microns 3.35 (C-H), 8.0, 8.4, 8.75, 8.95 (C-F), 9.6, 13.0. Figure 8 - H^1 NMR multiplets for CHBr, CH_2, CH, CH_2. Figure 9 - F^{19} NMR, Figure 10 - F^{19} NMR, Table XII - Mass spectrum m/e 445 (M^+), 369, 367 (M-Br), 287 (M-2Br), 273, 271, $(M-C_2F_3ClBr)$, 259, 257 $(M-C_3F_3ClBrH_2)$.

The reaction was repeated using a higher ratio of 1,2-dibromo-2-chlorotrifluoroethane to trifluoropropene with essentially the same results. There was no evidence of the presence of the 1 to 1 addition product but $\sim$25% of the 1,2-dibromo-2-chlorotrifluoroethane had added to two molecules of trifluoropropene to give $CF_2Br\overset{*}{C}FClCH_2CH(CF_3)CH_2\overset{*}{C}HBrCF_3$ (92 grams).

Addition of 1,2-Dichloro-2-iodotrifluoroethane ($CF_2Cl-CFClI$) to Trifluoropropene ($CH_2=CHCF_3$)

A three-liter autoclave was equipped with a 3,000 psi rupture disc and pressure checked at 800 psi with dry nitrogen before being evacuated to full vacuum. The autoclave was cooled in liquid oxygen before the 1,2-dichloro-2-iodotrifluoroethane (1,000 grams, 3.58 moles) and benzoyl peroxide (11 grams) was sucked into the evacuated system. The trifluoropropene (170 grams, 1.77 moles) was condensed in via a glass vacuum system. The mixture was heated at 100°C for four hours before being cooled to ambient temperature. Work-up showed that no reaction had occurred.

The three-liter autoclave reaction was repeated and the reactants heated to 150°C with rocking for four hours. After being cooled to room temperature and the volatiles collected, the liquid products were distilled to give $CF_2ClCFClI$ (685 grams, 2.16 moles), and the desired $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ (315 grams, .84 moles, bp 161-166°C) in 75% yield. The large boiling range is due to the presence of two sets of diastereomers. (Figures 51 - 54). Figure 51 - both diastereomers. IR (liquid) maxima in microns 3.30 (C-H), 7.6, 7.8, 8.05, 8.15, 8.45, 8.8 (C-F), 9.2, 10.0. Figure 52 - F^{19} NMR, three fluorines, doublet CF_3; two fluorines, CF_2Cl triplet; one fluorine, multiplet for CFCl; Figure 53 and C - H^1 NMR, complicated multiplet for both CH_2 and CHI, Table XXII - mass spectrum m/e 376, 374 (M^+), 291, 289 ($M-CF_2Cl$), 349, 247 (M-I), 213, 211 (M-I and Cl).

The reaction was repeated in a three-liter autoclave using the recovered $CF_2ClCFClI$ (685 grams, 2.16 moles) and trifluoropropene (170 grams, 1.77 moles) to give an additional 310 grams of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ in 80% distilled yield.

Preparation of 1-Bromo-2-iodotetrafluoroethane (CF_2BrCF_2I)

A three-liter autoclave was used to prepare the 1-bromo-2-iodotetrafluoroethane. After being pressure and vacuum checked and cooled to -196°C, the autoclave was charged with bromine (480 grams) and iodine (790 grams), and the tetrafluoroethylene was condensed in (1,100 grams). The reaction mixture was heated to 200°C for 20 hours with rocking before being cooled to ambient temperature. The overgases were vented and the liquid products distilled to give 1,2-dibromotetrafluoroethane (210 grams), 1-bromo-2-iodotetrafluoroethane (610 grams, bp 79-80°C, 23% distilled yield), 1,2-diiodotetrafluoroethane (360 grams) and 560 grams of a residue which contained higher telomers (Figure 11).

Addition of 1-Bromo-2-iodotetrafluoroethane (CF_2BrCF_2I) to Ethylene

A three-liter autoclave was equipped as in previous reactions, evacuated and cooled to -196°C before the benzoyl peroxide (15 grams) and 1-bromo-2-iodotetrafluoroethane (610 grams) were added. Ethylene (120 grams) was condensed into the autoclave and the system was warmed to 120°C for 16 hours with rocking. After cooling, the autoclave was vented and the liquid products distilled to give 1-bromo-2-iodotetrafluoroethane (151 grams), 1-bromo-4-iodo-1,1,2,2-tetrafluorobutane (286 grams, bp 160-161°C, 58% distilled yield), and 210 grams of higher boiling material (Figure 12).

Preparation of Olefins

Attempted Dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ with 50% Aqueous Sodium Hydroxide

A 500-ml, three-necked flask was equipped with a magnetic stirrer, a reflux condenser, a thermometer, and a dropping funnel. Aqueous sodium hydroxide (NaOH, 320 grams of 50%) was added to the flask and stirred as the mixture was heated to 80°C. The $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (169 grams, 0.53 moles) was added via the dropping funnel over a one-hour period. The organic material immediately formed a lower layer and did not react with the caustic solution.

Dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ with Potassium t-Butoxide and Dimethyl Sulfoxide

A 500-ml, three-necked flask was equipped with a mechanical stirrer, a condenser backed by a liquid oxygen cooled trap, a thermometer, and a dropping funnel. The potassium-t-butoxide (41 grams, 0.37 moles) and dimethyl sulfoxide (200 ml) were added to the flask and the mixture stirred. The fluorocarbon, $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (95 grams, 0.3 moles) was added dropwise via the dropping funnel and the mixture was heated to ∿130°C before a reflux was noted. The condenser was replaced with a distillation head and 65 grams of material was collected. Redistillation gave 52 grams of $CF_2BrCFClCH{=}CHCH_3$ (bp 133-134°C, 73% yield, Figures 13 - 15). Figure 13 - IR (liquid) maxima in microns 3.36 (C-H), 6.0 (C=C), 8.25, 8.3, 8.8, (C-F) 9.9, 10.4, 10.7, 11.2, 12.5, 14.0. Figure 14 - H^1 NMR. Two types of vinyl protons, two hydrogens; and a doublet, three hydrogens, for CH_3. Figure 15 - F^{19} NMR. Table XIII - mass spectrum m/e 238 (M^+), 159, 157 (M-Br), 203, 201, (M-Cl), 107 (M-Br, Cl and CH_3). High resolution mass spectrum, $C_5F_3H_5ClBr$, calculated mass 236.09, measured 235.92.

Dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ with Ethanolic Potassium Hydroxide

A 500-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermometer, and a condenser. Ethanol (250 ml) and potassium hydroxide (65 grams) were stirred until the base had gone into solution. The $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (320 grams, 0.95 moles) was added dropwise and an exotherm to 60°C was noted over a two-hour period. After being stirred for an additional three hours, the material was washed twice with one liter of ice water to give 230 grams of product. After the mixture was dried over molecular sieves, distillation gave 217 grams of $CF_2BrCFClCH{=}CHCH_3$ (88% yield, bp 133-134°C).

The dehydrohalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (329 grams, 1.03 moles) was repeated using potassium hydroxide (63 grams, 1.1 moles) in ethanol (600 ml). Distillation of the product gave $CF_2BrCFClCH{=}CHCH_3$ (bp 131-132°C, 181 grams, 74% yield).

Dehydrohalogenation of $CF_2BrCF_2CH_2CH_2I$ with Ethanolic Potassium Hydroxide

The attempted reaction of $CF_2BrCF_2CH_2CHI$ with aqueous sodium hydroxide gave only recovered starting material but alcoholic potassium hydroxide gave the desired olefin. A 250-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermowell, and a condenser before being charged with ethanol (150 ml) and potassium hydroxide (10 grams). The $CF_2BrCF_2CH_2CH_2I$ (61 grams, 0.19 moles) was added dropwise over a two-hour period. After the material was washed with 500 ml of ice water, the organic layer was collected and dried over molecular sieves. Distillation of the crude product (36 grams) gave 28 grams of 99+% pure $CF_2BrCF_2CH{=}CH_2$ (80% distilled yield, bp 64°C, Figures 16 - 18).

Dehydrohalogenation of $\mathrm{CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3}$ with Ethanolic Potassium Hydroxide

The dehydrohalogenation of $\mathrm{CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3}$ with ethanolic potassium hydroxide was attempted in a 250-ml, three-necked flask equipped with a magnetic stirrer, dropping funnel, thermometer, and condenser. The potassium hydroxide (18 grams, 0.32 moles) and ethanol (200 ml) were placed in the flask and stirred for 30 minutes. The $\mathrm{CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3}$ (100 grams, 0.22 moles) was added over a one-hour period and stirred for an additional two hours. After the material was washed with ice water (500 ml), the organic layer was collected and dried over molecular sieves. The product was the starting material which was recovered in 85% yield.

Dehydrohalogenation of $\mathrm{CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3}$ with Ethanolic Potassium Hydroxide

A one-liter, three-necked flask was equipped with a magnetic stirrer, dropping funnel, distillation head and thermowell. The potassium hydroxide (76 grams, 1.25 moles), water (225 ml), and ethanol (300 ml) were placed in the flask and stirred as the mixture was heated to 70°C. The $\mathrm{CF_3Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3}$ (300 grams, 0.8 moles) was added slowly via the dropping funnel as the mixture was heated to 80°C with material distilling from the reaction mixture. The product, $\mathrm{CF_2ClCFClCH{=}CHCF_3}$ (131 grams, bp 88°C), was washed with water and dried over molecular sieves. Distillation gave a 70% yield (Figures 55 - 58). Figure 55 - IR (liquid) maxima in microns 3.18 (C-H), 5.88 (C=C), 7.61, 7.8, 8.2, 8.6 (C-F), 9.3, 9.5, 10.3, 11.0, 11.5, 12.6. Figure 56 - F^{19} NMR, three fluorines, doublet for $\mathrm{CF_3}$;

two fluorines, doublet for CF_2Cl; one fluorine, multiplet for CFCl. Table XXIII - mass spectrum m/e 246 (M^+), 211 (M-Cl), 163, 161 ($M-CF_2Cl_2$).

The reaction was repeated using $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ (280 grams, 0.75 moles). The product was collected in 60% yield after being separated from the ethanol and dried over 4Å molecular sieves.

Decarboxylation of $CF_2ClCFBrCF_2CFBrCF_2COONa$

A one-liter, three-necked flask was equipped with a mechanical stirrer, thermometer, and a distillation head. The $CF_2ClCFBrCF_2CFBr$-CF_2COONa (400 grams, 0.84 moles) was placed in the flask along with diglyme (500 ml) and the mixture was heated to 90°C slowly with the evolution of CO_2. The mixture was then heated to a flask temperature of 145°C while the product distilled from the flask. The collected material contained the $CF_2ClCFBrCF_2CF{=}CF_2$ along with diglyme. The diglyme was washed from the mixture with ice water to give 190 grams of 98+% pure $CF_2ClCFBrCF_2CF{=}CF_2$ (bp 104-106°C, Figure 19). Figure 19 - IR (liquid) maxima in microns 5.6 ($CF_2{=}CF$), 7.4, 7.7, 8.7, 9.0 (CF), 9.6, 10.2, 11.0, 11.2, 11.6, 123, 12.7, 13.5.

The Dehalogenation of $CF_2Br\overset{*}{C}FClCH{=}CHCH_3$ with Zinc

A one-liter, three-necked flask was equipped with a mechanical stirrer, a dropping funnel, a thermometer, and a Vigreux column with a distillation head. The zinc (65 grams, 1.01 moles) and ethanol (250 ml) were placed in the flask and stirred while being heated to 65°C. The $CF_2BrCFClCH{=}CHCH_3$ (210 grams, 0.88 moles) was added dropwise via the dropping funnel over a one-hour period with the product distilling out as it was formed. The product, $CF_2=CFCH=CHCH_3$, was collected (85 grams, 97% pure, bp 44-45°C, 78% yield, Figures 20 - 23). Figure 20 - IR (liquid) maxima in microns 3.4 (C-H), 5.6 ($CF_2=CF$), 6.05 (CH=CH), 7.8, 7.95, 8.5, 9.0 (C-F), 9.5, 10.5. Figure 22 - H^1 NMR, three hydrogens, doublet (CH_3); two hydrogens, multiplet (CH=CH). Figure 23 - F^{19} NMR, three fluorines, four sets of multiplets. Table XIV - mass spectrum m/e 122 (M^+), 121 (M-H), 103, (M-F), 102 (M-HF), 109 ($M-H_2F$), 72 ($M-CF_2$). High resolution mass spectrum, $C_5F_3H_5$, calculated mass 122.09, measured 122.03.

The reaction was repeated using $CF_2BrCFClCH=CHCH_3$ (40 grams), zinc (40 grams), and ethanol (150 ml). The product was collected, washed with ice water, dried over molecular sieves and distilled to give 19 grams of $CF_2=CFCH=CHCH_3$ (bp 44-45°C, 92% yield).

The preparation of $CF_2=CFCH=CHCH_3$ was repeated using $CF_2BrCFClCH=CHCH_3$ (145 grams, 0.61 moles), zinc (46 grams, 0.69 moles) and ethanol (150 ml). The product which distilled from the reaction mixture, washed twice with ice water and dried over molecular sieves gave $CF_2=CFCH=CHCH_3$ (69 grams, 92% yield, bp 44-45°C).

Dehalogenation of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ with Zinc

A 500-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermometer, and a Vigreux column with a distillation head. The zinc (76 grams, 1.19 moles) and ethanol (250 ml) were placed in the flask and heated to 45°C with stirring before the fluorocarbon was added dropwise. An exothermic reaction ensued and the temperature rose to 80°C. After being stirred for one and one-half hours, the liquid was decanted into one-liter of water and the organic layer was separated and dried. Distillation gave $CF_2{=}CFCH_2CHBrCH_3$ (67 grams, bp 110-111°C, 91% yield, Figures 24 - 26). Figure 24 - IR (liquid) maxima in microns 3.38, 3.45 (C-H), 5.61 ($CF_2{=}CF$), 7.8, 8.0, 8.2, 8.6 (C-F), 9.0, 9.4, 9.6, 9.8, 10.2. Figure 25 - F^{19} NMR, three fluorines, three sets of multiplets for $CF_2{=}CF$, Figure 26 - H^1 NMR, three hydrogens, doublet for CH_3; two hydrogens, two sets of multiplets for CH_2; one hydrogen, sextet for CHBr. Table XV - mass spectrum m/e 204, 202 (M^+) 123 (M-Br), 109, 107 ($M-C_3F_7H_2$), 103 (M-H, F, Br), 95 ($M-C_2H_7Br$). High resolution mass spectrum, $C_5F_3H_6Br$, calculated mass 202.10, measured 201.96.

Dehalogenation of $CF_2Br\overset{*}{C}FClCH_2CH(CF_3)CH_2\overset{*}{C}HBrCF_3$ with Zinc

A 250-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermometer, and a distillation head. The ethanol (150 ml) and zinc (20 grams, 0.31 moles) were added to the flask and stirred as a few drops of bromine were added to activate the zinc. The mixture was heated to 50°C before the $CF_2Br\overset{*}{C}FClCH_2CH(CF_3)CH_2\overset{*}{C}HBrCF_3$ (31 grams, 0.066 moles) was added via the dropping funnel. An exotherm was immediately noted and distillation gave ethanol and fluorocarbon product. After being washed with ice water to remove the ethanol, the organic layer was separated, dried over molecular sieves and distilled to give $CF_2{=}CFCH_2CH(CF_3)CH_2CH{=}CF_2$ (bp 134-138°C, 95% yield, 16 grams, Figures 27 and 28). Figure 27 - IR (liquid) maxima in microns 3.38 (C-H), 5.55 ($CF_2{=}CF$), 5.7 ($CF_2{=}CH$), 7.7, 8.0, 8.4, 8.5, 9.0 (C-F). Figure 28 - F^{19} NMR, three fluorines, singlet CF_3; two fluorines, multiplet ($CF_2{=}CH$); three fluorines, multiplet ($CF_2{=}CF$).

Dehalogenation of $CF_2Cl\overset{*}{C}FBrCF_2CF=CF_2$ with Zinc

A one-liter, three-necked flask was equipped with a magnetic stirrer, Vigreux column, thermometer, and dropping funnel. A distillation head backed by a liquid oxygen trap was used to collect the product. The zinc (60 grams, 0.94 moles), ethanol (500 ml), and bromine (3 ml) were added to the flask and stirred as the mixture was heated to 50°C. The $CF_2ClCFBrCF_2CF=CF_2$ (190 grams, 0.58 moles) was added dropwise via the dropping funnel as the product was collected in the distillation head. After the product was washed with ice water, the organic material was dried over molecular sieves and distilled to give $CF_2=CFCF_2CF=CF_2$ (92 grams, 75% yield, bp 36-38°C, Figures 29 - 30). Figure 29 - IR (liquid) maxima in microns 5.6 ($CF_2=CF$), 7.4, 7.6, 7.8, 8.35, 8.42, (C-F), 9.7, 10.8, 11.2. Figure 30 - F^{19} NMR, eight fluorines, six sets of multiplets for the $(CF_2=CF)_2CF_2$. Table XVI - mass spectrum m/e 212 (M^+), 162 ($M-CF_2$), 143 ($M-CF_3$), 131 ($M-C_2F_3$), 93, ($M-C_2F_5$). High resolution mass spectrum, C_5F_8, calculated mass 212.04, measured 211.99.

Dehalogenation of $CF_2ClCFClCH=CHCF_3$ with Zinc

A 250-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, distillation head, and a thermometer. The zinc (40 grams) and ethanol (150 ml) were placed in the flask and stirred as bromine (1 ml) was added to activate the zinc. The mixture was heated to 65°C before the olefin $CF_2ClCFClCH=CHCF_3$ (90 grams, 0.36 moles) was added dropwise. The product immediately distilled from the reaction mixture and, after the material was washed with ice water and dried over molecular sieves, the $CF_2=CFCH=CHCF_3$ (59 grams, bp 43-44°C, 92% yield) was distilled. (Figures 57 - 59). Figure 57 - IR (liquid) maxima in microns 3.35 (C-H), 5.7 ($CF_2=CF$), 5.95 (CH=CH), 7.58, 7.7, 7.8, 8.7 (C-F), 10.3, 12.0. Figure 58 - F^{19} NMR, three fluorines, singlet for CF_3, three fluorines, three sets of multiplets for ($CF_2=CF$). Figure 59 - H^1 NMR, two hydrogens, complex multiplet for CH=CH. Table XXIV - mass spectrum m/e 176 (M^+), 157 (M-F), 126 (M-CF_2), 107 (MCF_3). High resolution mass spectrum, $C_5F_6H_2$, calculated mass 176.07 measured 176.01.

The reaction was repeated using 55 grams of $CF_2ClCFClCH=CHCF_3$ to give 31 grams of $CF_2=CFCH=CHCF_3$ for a 80% distilled yield.

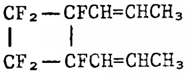
Dehalogenation of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$ with Zinc

A 250-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, short column, distillation head, and thermometer. The flask was charged with ethanol (150 ml) and zinc (20 grams) and the mixture stirred and one ml. of bromine was added. The mixture was heated to 50°C as the $CF_2\overset{*}{C}lCFClCH_2\overset{*}{C}HICF_3$ (90 grams) was added dropwise and an immediate exotherm to 80°C was noted. After the mixture was allowed to cool to ambient temperature, the solution was added to one liter of ice water. The organic layer was collected and dried before distillation. The product, $CF_2ClCFClCH_2CH=CF_2$ (37 grams, 72% yield), was distilled (bp 101-103°C) and was 99+% pure by GLC analysis (Figures 80 and 81). Figure 80 - IR (liquid) maxima in microns 5.67 ($CF_2=CH$), 7.55, 7.9, 8.15, 8.4, 8.62, 9.1, (C-F), 9.3, 9.9, 12.3. Figure 81 - F^{19} NMR, two fluorines, multiplet for ($CF_2=CH$), two fluorines, doublet for CF_2Cl, one fluorine, multiplet for CFCl. Table XXXII - Mass spectrum m/e 230 (M^+), 193 (M-Cl), 143, (M-CF_2Cl), 77 (M-$C_2F_3Cl_2$). High resolution mass spectrum, $C_5F_5{}^{35}Cl_2H_3$, calculated mass 228.07, measured 227.95, $C_5F_5{}^{35}Cl{}^{37}ClH_3$, calculated mass 230.07, measured 229.95.

Reactions of Olefins Prepared

2 + 2 Reactions of Chlorotrifluoroethylene with CF_2=CFCH=$CHCH_3$

An ampoule was charged with one gram of CF_2=CFCH=$CHCH_3$ and cooled in liquid oxygen before a full vacuum was applied and one gram of chlorotrifluoroethylene was condensed into the system. The ampoule was sealed under vacuum and placed in an oil bath at 160°C for 20 hours. After it was cooled to ambient temperature, the ampoule was frozen in liquid oxygen and opened. The overgases were vented and 1.2 grams of product was collected. Infrared analysis indicated a R'CH=CHR absorption. A larger sample was then prepared using 6.1 grams of CF_2=CFCH=$CHCH_3$ and 5.8 grams of chlorotrifluoroethylene. The product was completely characterized as the dimer of CF_2=CFCH=$CHCH_3$ with the following 2 + 2 structure (bp 160-161°C, quantitative yield,



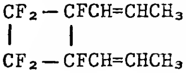
Figures 31 - 33). Figure 31 - IR (liquid) maxima in microns 3.35, 3.41 (C-H), 5.95 (CH=CH), 7.2, 7.25, 7.9, 8.4 (C-F), 10.1, 10.4, 11.2. Figure 32 - H^1 NMR, three hydrogens, doublet for CH_3; two hydrogens, two sets of multiplets for (CH=CH). Figure 33 - F^{19} NMR, two fluorines, two sets of multiplets for CF's; four fluorines, five sets of multiplets for both CF_2's. Table XVII - Mass spectrum m/e 244 (M^+), 122 (M-$C_5F_3H_3$).

2 + 2 Cycloaddition of 2,2-Dichlorodifluoroethylene with $CF_2{=}CFCH{=}CHCH_3$

An ampoule was charged with $CF_2{=}CFCH{=}CHCH_3$ (6.1 grams, 0.05 moles) and frozen in liquid oxygen while being evacuated to full vacuum. The $CF_2{=}CCl_2$ (6.7 grams, 0.05 moles) was condensed into the ampoule and the system sealed under vacuum. After reacting for 16 hours at 160°C in an oil bath, the tube was opened and the overgases vented. The only product isolated was the 2 + 2 cyclic dimer of $CF_2{=}CFCH{=}CHCH_3$.

Dimerization of $CF_2{=}CFCH{=}CHCH_3$

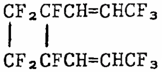
An ampoule was charged with $CF_2{=}CFCH{=}CHCH_3$ (15 grams) and evacuated after being cooled in liquid oxygen. The system was sealed under vacuum and heated in an oil bath at 100°C for 16 hours. When the ampoule was opened, the dimer was the only product present.



$$\begin{array}{l} CF_2 - CFCH{=}CHCH_3 \\ \,| \qquad | \\ CF_2 - CFCH{=}CHCH_3 \end{array}$$

Dimerization of $CF_2{=}CFCH{=}CHCF_3$

A 50-ml ampoule was charged with $CF_2{=}CFCH{=}CHCF_3$ (4.4 grams, 0.025 moles) sealed and heated to 80°C for 20 hours. After being cooled to ambient temperature, the ampoule was opened. Infrared analysis indicated some unreacted diene. A GLC analysis showed the material to be 50% unreacted diene and 50% 2 + 2 cyclic dimer.

The reaction was repeated at 100°C for 20 hours to give complete conversion of $CF_2{=}CFCH{=}CHCF_3$ to the dimer  $\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ |\;\;| \\ CF_2CFCH{=}CHCF_3 \end{array}$ (bp 133-135°C Figures 63 and 64). Figure 63 - IR (liquid) maxima in microns 3.18

(C-H), 5.85 (CH=CH), 7.55, 7.8, 8.3, 8.75 (C-F), 10.4, 10.7. Figure 64 - F^{19} NMR, three fluorines, doublet for CF_3, two fluorines, two sets of multiplets for CF's; four fluorines, six sets of multiplets for CF_2's. Table XXVI - Mass spectrum 352 (M^+), 176 ($M-C_5F_6H_2$), 157 ($M-C_5F_7H_2$), 126 ($M-C_6F_8H_2$).

Co-dimerization of $CF_2=CFCH=CHCH_3$ with $CF_2=CFCH=CHCF_3$

A 50-ml ampoule was charged with $CF_2=CFCH=CHCH_3$ (2 grams) and $CF_2=CFCH=CHCF_3$ (3 grams) before being sealed and heated to 105°C for 20 hours. The ampoule was cooled to ambient temperature, and the ampoule was opened. Infrared analysis showed no $CF_2=CF-$ absorption. Distillation gave three fractions, the 2 + 2 cyclic dimer of $CF_2=CFCH=CHCF_3$, the co-dimer of $CF_2=CFCH=CHCF_3$ and $CF_2=CFCH=CHCH_3$, and the 2 + 2 cyclic dimer of $CF_2=CFCH=CHCH_3$ (Figures 65 and 66). Figure 65 - IR (liquid) maxima in microns 3.18, 3.3, 3.35, (C-H), 5.88 (CH=CH), 7.1, 7.6, 7.8, 8.38, 8.7, (C-F), 10.3, 10.7. Figure 66 - F^{19} NMR, three fluorines, doublet for CF_3; four fluorines, multiplets for CF_2 in cyclobutane; two fluorines, multiplets for CF in cyclobutane. Table XXVII - Mass spectrum m/e 298 (M^+), 176 ($M-C_5F_3H_5$), 122 ($M-C_5F_7H_2$).

Attempted 2 + 2 Cycloaddition of Chlorotrifluoroethylene with $CF_2=CFCH_2CHBrCH_3$

An ampoule was charged with $CF_2=CFCH_2CHBrCH_3$ (10.1 grams, 0.05 moles), which was frozen and evacuated, before the chlorotrifluoroethylene (5.8 grams, 0.05 moles) was condensed into the system. After the ampoule was heated for 20 hours at 140°C in an oil bath, it was opened and the overgases vented. The only product isolated was the starting CF_2=$CFCH_2CHBrCH_3$.

The reaction of CF_2=$CFCH_2CHBrCH_3$ with chlorotrifluoroethylene was repeated at 160°C with similar results. No 2 + 2 addition was found and the olefin, CF_2=$CFCH_2CHBrCH_3$, was recovered.

Attempted Reaction of Butadiene with CF_2=$CFCH_2CHBrCH_3$

An ampoule was charged with butadiene (0.84 grams) and CF_2=$CFCH_2CHBrCH_3$ (4.06 grams). The ampoule was sealed and heated to 125°C for 20 hours. After cooling to room temperature the ampoule was opened and the CF_2=$CFCH_2CHBrCH_3$ was recovered unreacted.

The reaction was repeated using a large excess of butadiene (3.36 grams) with no reaction again after 20 hours at 120°C.

Attempted Reaction of Butadiene with CF_2=$CFCH$=$CHCH_3$

A 500-ml ampoule was charged with CF_2=$CFCH$=$CHCH_3$ (6.1 grams, 0.05 moles) and butadiene (5.4 grams, 0.1 moles) before being heated to 120°C for four hours. A fog was noted after one hour and black solids had formed after four hours and the reaction was worked-up. After the excess butadiene was removed, the only liquid product collected was the 2 + 2 cyclodimer of the pentadiene.

Radical Addition of Bromotrichloromethane to CF_2=$CFCH_2CHBrCH_3$ with Benzoyl Peroxide

An ampoule was charged with bromotrichloromethane (9.9 grams), CF_2=$CFCH_2CHBrCH_3$ (10.0 grams) and benzoyl peroxide (0.4 grams). After being cooled to -196°C, the ampoule was evacuated to full vacuum and sealed. The system was heated in an oil bath at 160°C for 16 hours before being opened and the products collected. Distillation gave 9.1 grams of material (bp 80-88°C/0.1 mm) which showed two peaks by GLC analysis. Analysis showed the product to be two sets of diastereomers of $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$ (79% yield, Figures 34 - 34). Figure 34 - IR (liquid) maxima in microns 3.31, 3.38 (C-H), 8.3, 8.5, 8.7, 9.1, (C-F) 9.7, 10.1, 11.7, 11.9, 12.0. Figure 36 - H^1 NMR, three hydrogens, doublet for CH_3; two hydrogens, multiplets for CH_2; one hydrogen, multiplet for CHBr. Figure 37 - F^{19} NMR, two fluorines, two sets of doublets for CF_2; one fluorine, two sets of multiplets for CF. Table XVIII - Mass spectrum m/e 398, 400, 402 M^{+}), 323, 321, 319 (M-Br), 287, 285, 283 (M-Br+Cl). High resolution mass spectrum, $C_6H_5{}^{35}Cl_3F_3{}^{79}Br_2$, calculated mass 397.10, measured mass 397.79.

Radical Addition of CCl_3Br with $CF_2{=}CFCH{=}CHCH_3$ Using Benzoyl Peroxide

A 500-ml ampoule was charged with bromotrichloromethane, CCl_3Br, (197 grams, 1 mole), benzoyl peroxide (2 grams) and the pentadiene, $CF_2{=}CFCH{=}CHCH_3$, (12.2 grams, 0.1 mole). The mixture was heated to 70°C for four hours before being placed in a distillation flask and the CCl_3Br removed. The remaining material (14 grams) was further distilled on a micro-column to give the 2 + 2 cyclodimer (7 grams) and the desired adduct $CCl_3CF_2CFBrCH{=}CHCH_3$ (6 grams, bp 225-230°C Figures 60 - 62). Figure 60 - IR (liquid) maxima in microns 3.3 (C-H), 5.85 (CH=CH), 7.6, 7.9, 8.7 (C-F), 9.5, 11.5, 11.8, 12.6, 13.4. Figure 61 - F^{19}, two fluorines, two multiplets for CF_2; one fluorine, two multiplets for CF. Figure 62 - H^1 NMR, three hydrogens, two doublets for CH_3; two hydrogens, two multiplets for vinyl hydrogens. Table XXV - Mass spectrum m/e no parent peak, 241, 239, (M-Br), 203, 201 (M-CCl_3), 151 (M-CCl_3CF_2-CF_2), 122 (M-Br, CCl_3, 107 (M-Br, CCl_3) CH_3). High resolution mass spectrum, $C_6H_5F_3{}^{35}$-$Cl_3{}^{79}Br$, calculated mass 318.10, measured 317.96.

Radical Addition of CCl_3Br with CF_2=CFCH=$CHCF_3$ Using Benzoyl Peroxide

A 100-ml ampoule was charged with CCl_3Br (19.8 grams, 0.1 mole) benzoyl peroxide (0.2 grams) and CF_2=CFCH=$CHCF_3$ (4.4 grams, 0.025 moles) before being heated to 80°C for 20 hours. The material was then distilled on a micro column to give 3.6 grams of higher boiling material. NMR analysis indicated higher telomers and no simple adduct.

2 + 2 Cycloaddition Reaction of Chlorotrifluoroethylene with CF_2=$CFCF_2CF$=CF_2

The attempted cycloaddition reaction of chlorotrifluoroethylene with CF_2=$CFCF_2CF$=CF_2 was carried out in an ampoule at 160°C for 48 hours. The CF_2=CFCl (5.8 grams,0.05 moles) and F,1,4-pentadiene (10.6 grams, 0.05 moles) were placed in the ampoule, sealed, and heated to 160°C. After the ampoule was opened and the overgases vented, the starting material, CF_2=$CFCF_2CF$=CF_2, was recovered.

The Addition of Bromine to CF_2=$CFCF_2CF$=CF_2

A 50-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermometer, and a condenser. The CF_2=$CFCF_2CF$=CF_2 (10.6 grams, 0.05 moles) was placed in the flask and stirred as the bromine (8.0 g) was added dropwise via the dropping funnel. As the reaction proceeded, the temperature rose to 50°C and the flask was cooled in a water bath. After the bromine had been added, the mixture was distilled to give the dibromide $CF_2BrCFBrCF_2CF{=}CF_2$ (76% yield, 14 grams, bp 126-127°C, Figures 38 and 39). Figure 38 - IR (liquid) maxima in microns 5.6 ($CF_2{=}CF$), 7.4, 7.65 ($CF_2{=}CF$), 8.5, 9.0 (C-F), 9.5, 10.4, 11.7. Figure 39 - F^{19} NMR, two fluorines, triplet for ($CF_2{=}C$); one fluorine, multiplet for (CF=C); two fluorines, a doublet of doublets for center CF_2; one fluorine, a multiplet for CFBr; two fluorines and two multiplets for CF_2Br.

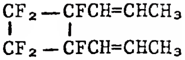
The Attempted Radical Addition of 2-Iodoheptafluoropropane with $CF_2{=}CFCF_2CF{=}CF_2$

An ampoule was loaded with 2-iodoheptafluoropropane (14.8 grams, 0.05 moles) and $CF_2{=}CFCF_2CF{=}CF_2$ (10.6 grams, 0.05 moles) before being cooled to -196°C in liquid oxygen and evacuated. After being sealed, the ampoule was warmed to 155°C for 36 hours. The pentadiene, $CF_2{=}CFCF_2CF{=}CF_2$, and CF_3CFICF_3 were the only products recovered.

The Attempted Reaction of Trifluoronitrosomethane with $CF_2{=}CFCF_2CF{=}CF_2$

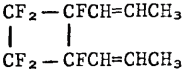
An ampoule was charged with $CF_2{=}CFCF_2CF{=}CF_2$ (4.2 grams, 0.02 moles) before being cooled in liquid oxygen and evacuated. Trifluoronitrosomethane (CF_3NO, 2.0 grams, 0.02 moles) was condensed into the ampoule and the system sealed. The ampoule was allowed to warm to -78°C in a Dry-Ice acetone bath over a 48-hour period. Since the deep blue color of CF_3NO still remained, the ampoule was warmed to 0°C for an additional 48 hours, then to ambient temperature for eight hours. When the ampoule was opened, the only products recovered were trifluoronitrosomethane and $CF_2{=}CFCF_2CF{=}CF_2$.

The Reaction of Ozone with



$$\begin{array}{l} CF_2\text{—}CFCH{=}CHCH_3 \\ \;|\qquad\;\; | \\ CF_2\text{—}CFCH{=}CHCH_3 \end{array}$$

A 250-ml Erylenmeyer flask was equipped with a gas inlet tube and a outlet which was vented to the outside. The dimer,



$$\begin{array}{l} CF_2\text{—}CFCH{=}CHCH_3 \\ \;|\qquad\;\; | \\ CF_2\text{—}CFCH{=}CHCH_3 \end{array}$$

(25 grams, 0.12 moles) was dissolved in methylene chloride (150 ml) and placed in the reactor. Ozone, from a Welback ozone generator, was bubbled through the mixture for three hours at $\sim$2% ozone concentration (2.5 equivalents of ozone) after the solution had been cooled to -78°C in a Dry-Ice acetone bath. After removal of the methylene chloride, a water white semi-viscous fluid remained which contained none of the starting material. The reactivity of this material with potassium iodide indicated the presence of the ozonide (Figures 40 and 41).

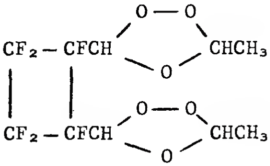


Figure 40 - IR (liquid) maxima in microns 3.3, 3.38 (C-H), 7.2, 7.9, 8.3, 8.9, 9.1 (C-F), 11.2. Figure 41 - H^1 NMR, three hydrogens, doublet for CH_3; two hydrogens, multiplet for CH.

An attempt to decompose the ozonide with zinc and acetic acid became a run-away reaction after ∿20 minutes and only polymeric tars remained.

The Reaction of Ethanol and Potassium Hydroxide with $CF_2=CFCH=CHCH_3$

A 100-ml, three-necked flask was equipped with a magnetic stirrer, thermometer, dropping funnel, and a condenser backed by a liquid oxygen trap. The ethanol (50 ml) and potassium hydroxide (6 grams, 0.12 moles) were added to the flask and stirred as the $CF_2=CFCH=CHCH_3$ (11.2 grams, 0.1 moles) was added dropwise. An exotherm to 35°C was noted and, after one hour, the mixture was washed with ice water (500 ml). The lower organic layer was collected and dried over molecular sieves and distilled to give 9.2 grams of a mixture of $CH_3CH_2OCF_2CFHCH=CHCH_3$ (80%) and $CH_3CH_2OCF_2CF=CHCH_2CH_3$ (20%) (bp 125-129°C, Figures 42 - 44). Figure 42 - IR (liquid) maxima in microns 3.35 (C-H), 5.8 (CF=CH), 5.92 (CH=CH), 7.7, 7.82, 8.2, 8.7 - (C-F), 9.5 - (C-O), 10.3. Figure 43 - H^1 NMR, three hydrogens, doublet for CH_3; three hydrogens, triplet for CH_3; two hydrogens, multiplet for CH_2; three hydrogens, three types of vinyl hydrogens. Figure 44 - F^{19} NMR, one fluorine, multiplet for (CF=C); one fluorine, multiplet for (CFH); two fluorines, multiplet for (CF_2). Table XIX - Mass spectrum m/e 168 (M^+), 153 $(M-CH_3)$, 151 $(M-CH_5)$, 139 $(M-C_2H_5)$, 148 (M-HF), 123 $(M-C_2H_5O)$.

The Reaction of Ethanol and Potassium Hydroxide with $CF_2=CFCH=CHCF_3$

A 50-ml, three-neck flask was equipped with a thermometer, reflux condenser, dropping funnel, and magnetic stirrer. The ethanol

(20 ml) and potassium hydroxide (0.5 grams) were placed in the flask and stirred over a 20-minute period. The $CF_2=CFCH=CHCF_3$ (8.8 grams) was added via the dropping funnel over a 20-minute period with an exotherm to 56°C noted. After being cooled to room temperature, the mixture was added to 100 ml of ice water and the organic layer collected and dried over molecular sieves. Distillation gave 5.3 grams of product, $CH_3CH_2OCF_2CF=CHCH_2CF_3$ (bp 103-105°C, Figures 67 - 69). Figure 67 - IR (liquid) maxima in microns 3.3 (C-H), 5.78 (CH=CH), 7.6, 7.8, 7.95, 8.2, 8.65, (C-F), 9.3, 9.6 (C-O). Figure 68 - F^{19} NMR three fluorines, multiplet for (CF_3). Figure 69 - H^1 NMR, three hydrogens, triplet (CH_3); two hydrogens, multiplet (CH_2-O); one hydrogen, multiplet (CH=C); two hydrogens, multiplet (CH_2).

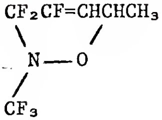
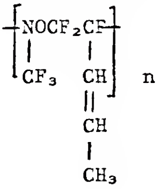
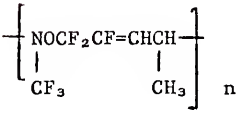
Addition of Bromine to $CF_2=CFCH=CHCH_3$

A 50-ml, three-necked flask was equipped with a magnetic stirrer, dropping funnel, thermometer, and reflux condenser backed by a liquid oxygen trap. The diene, $CF_2=CFCH=CHCH_3$, (2.6 grams, 0.021 moles) was placed in the flask and cooled in an ice water bath to +3°C. The bromine (3 grams) was added dropwise and a very vigorous reaction observed. The exotherm reached 40°C and was controlled by the rate of addition of bromine. There was collected 5.3 grams of product, $CF_2BrCFBrCH=CHCH_3$, which was distilled to give 4.2 grams of pure product (bp 152-155°C, Figures 45 and 46). Figure 45 - IR (liquid) maxima in microns 3.34, 3.4 (C-H), 5.9 (CH=CH), 7.7, 8.0, 8.4, 8.8 (C-F), 9.3, 9.7, 10.0, 10.6, 11.2, 11.7, 13.0. Figure 46 - H^1 NMR, three hdrogens, doublet for CH_3; two hydrogens, two types of vinyl hydrogen. Table XV - Mass spectrum m/e 283, 282 (M^+), 203, 201 (M-Br), 153, 151 (M-CF_2Br), 122 (M-Br_2).

Addition of Bromine to $CF_2=CFCH=CHCF_3$

A 50-ml, three-necked flask was placed in an ice water bath and equipped with a magnetic stirrer, condenser, thermowell, and dropping funnel. The diene, $CF_2=CFCH=CHCF_3$ (8.8 grams, 0.05 mole) was placed in the flask and cooled to 0°C before the bromine (8 grams) was added via the dropping funnel. The reaction was slow and, after one hour, the color had disappeared. Infrared analysis indicated the 1,4-addition product had been formed. NMR analysis proved the mixture to be a 75/25 ratio of 1,4- to 1,2-addition (bp 124-126°C, Figures 70 and 71). Figure 70 - IR (liquid) maxima in microns 3.15, 3.28 (C-H), 5.8 CF=CH, 5.85 (CH=CH, 7.5, 7.6, 7.95, 8.3, 8.6, 8.7 (C-F), 9.4, 10.6, 11.1, 13.5. Figure 71 - F^{19} NMR, three fluorines, two multiplets for (CF_3); two fluorines, two multiplets for (CF=C) and (CFBr); three fluorines, two multiplets for (CF_3). Table XXVIII - mass spectrum m/e 336 (M^+), 257, 255 (M-Br), 238, 236 (M-FBr), 186 (M-Br-CF_3). High resolution mass spectrum $C_5F_6H_2{}^{79}Br_2$, calculated mass 334.07, measured 333.84.

The Reaction of Trifluoronitrosomethane with $CF_2=CFCH=CHCH_3$ at -78°C

An ampoule was charged with $CF_2=CFCH=CHCH_3$ (2.25 grams, 0.02 moles) before being cooled with liquid oxygen to -196°C and evacuated. The trifluoronitrosomethane (CF_3NO, 2.0 grams, 0.02 moles) was condensed into the ampoule and the system sealed. The ampoule was then placed in a Dry-Ice acetone bath at -78°C for 48 hours. A green, thick oil was present; therefore, the ampoule was opened and the overgases were vented. The product, a slightly yellow viscous liquid, was recovered (3.1 gram) and placed in a 5-ml flask. A full vacuum was applied to remove the lower boiling component which was identified as  $\underset{\mathrm{N(CF_3)-O}}{\mathrm{CF_2CF{=}CHCHCH_3}}$ (2.0 grams), the 2 + 4 cycloaddition product. The remaining polymeric material contained two types of olefin absorptions as characterized by infrared analysis. Both  $\left[\mathrm{N(CF_3)OCF_2CF(CH{=}CHCH_3)}\right]_n$ 1,2 addition product and  $\left[\mathrm{N(CF_3)OCF_2CF{=}CHCH(CH_3)}\right]_n$ 1,4 addition product of the polymer were found to be present (Figures 47 - 49). Figure 47 - IR (liquid) maxima in microns, 3.32 (C-H), 5.85 (CF=C), 7.2, 7.7, 7.93, 8.3, 8.4, 8.8 (C-F), 9.25, 9.6, 11.0, 13.6. Figure 48 - H^1 NMR, three hydrogens, doublet for (CH_3); one hydrogen, multiplet for (CH-O); one hydrogen, vinyl hydrogen multiplet. Figure 49 - F^{19} NMR, three fluorines, multiplet for (CF_3-N); one fluorine, quartet for (CF=C); two fluorines, multiplet for (CF_2-N). Table XXI - Mass spectrum m/e 221 (M^+), 122 (M-CF_3NO), 121 (M-CF_3NOH). Figure 53 - 1,2 and 1,4 polymer with CF_3NO. High resolution mass spectrum, $C_6H_5F_6NO$, calculated mass 221.11, measured 221.03.

The Reaction of Trifluoronitrosomethane (CF_3NO) with $CF_2=CFCH=CHCF_3$ at −78°C

A 50-ml ampoule was charged with CF_3NO, trifluoronitrosomethane, (2 grams) and $CF_2=CFCH=CHCF_3$ (3.52 grams). The ampoule was sealed and the mixture placed in a Dry-Ice acetone bath for 24 hours. The ampoule was then opened and the products collected (5.1 gram). Distillation gave the 2 + 4 cycloaddition product (bp 100-102°C, 2.2 gram) and polymer (1.4 grams, Figures 72 - 75). Figure 72 - IR (liquid) maxima in microns 3.2 (C-H), 5.85 (CF=CH), 7.8, 8.3, 8.7, 8.8 (C-F), 10.7, 11.1. Figure 73 - IR (liquid) maxima in microns 3.16 (C-H), 5.85, (CF=CH), 6.2 (CH=CH), 7.5, 8.0 - 9.0 (C-F), 8.3, 10.2, 10.7. Figure 74 - H^1 NMR, one hydrogen, multiplet for (CH-O); one hydrogen, doublet of pentets for vinyl hydrogen. Figure 75 - F^{19} NMR, three fluorines, multiplet for (CF_3-N); one fluorine, multiplet for (CF=CH); two fluorines, multiplet for (CF_2-); three fluorines, multiplet for (CF_3-C). Table XXIX - Mass spectrum m/e 275 (M^+), 256 (M-F), 206 (M-CF_3), 176 (M-CF_3NO), 126 (M-CF_3NO, CF_2). High resolution mass spectrum, $C_6H_2F_9NO$, calculated mass 275.08, measured 275.00.

The Reaction of Phenylmagnesium Bromide with $CF_2=CFCH=CHCH_3$

A 250-ml, three-necked flask was equipped with a magnetic stirrer, thermometer, reflux condenser, and a dropping funnel. The flask was set up in an ice water bath before the ethyl ether (150 ml) and $CF_2=CFCH=CHCH_3$ (12.2 grams, 0.1 moles) were added. The mixture was stirred as the phenylmagnesium bromide (0.1 mole) was added over a 30-minute period. The temperature did not increase as had been expected. After being stirred for five hours, the mixture was hydrolyzed in ice water, the ether layer was collected and dried over molecular sieves. The ethyl ether was removed to give 5 grams of higher boiling material which was vacuum distilled to give 2.1 grams of a mixture of biphenyl, phenol, and 1.2 grams of the desired product $C_6H_5CF{=}CFCH{=}CHCH_3$ (Figure 76). Figure 76 - IR (liquid) maxima in microns 3.22, 3.25, 3.32, (C-H), 5.8 - CF=CF, 6.2 (C_6H_5), 8.0 - 8.4 (C-F), 13, 14 aromatic. Table XXX - Mass spectrum m/e 180 ($\dot{M}^+$), 179 (M-H), 165 (M-CH_3), 154 (M-C_2H_2), 153 (M-C_2H_3), 152 (M-C_2H_4).

The Reaction of Phenylmagnesium Bromide with $CF_2{=}CFCH{=}CHCF_3$

A 100-ml, three-necked flask was equipped with a magnetic stirrer, a thermometer, a reflux condenser, and a dropping funnel. The ethyl ether (30 ml) and $CF_2{=}CFCH{=}CHCF_3$ (8.8 grams, 0.05 moles) were placed in the flask and stirred as the phenylmagnesium bromide (0.05 moles) was added dropwise via the dropping funnel. There was an immediate exotherm to 50°C with vigorous reflux of the ether. The addition was carried out over a 30-minute period and, after one hour of stirring, the solution was hydrolyzed in ice water. The ether layer was collected, dried over molecular sieves and the ether removed. Further vacuum distillation gave the desired $C_6H_5CF{=}CFCH{=}CHCF_3$ (8 grams, bp 60-65/0.1 mm, 68% distilled yield). A GLC indicated two isomers, cis and trans in a 65/35 ratio (Figures 77 and 78). Figure 77 - IR (liquid) maxima in microns. 3.18, 3.32 (C-H), 5.95 (CF=CF), 6.19 (aromatic), 7.6, 7.8, 7.9, 8.8 (C-F), 10.2, 12.9, 14.1. Figure 78 - F^{19} NMR, three fluorines, multiplet for (CF_3); two fluorines, multiplets for (CF=CF) both cis and trans. Table XXXI - Mass spectrum m/e 235, 234 (M^+), 165 (M-CF_3), 164 (M-CF_3, H), 145 (M-CF_3, HF). High resolution mass spectrum $C_{11}H_7F_5$, calculated 234.17, measured 234.05.

The reaction was repeated at -30°C using the same ratio of starting material. The hydrolysis was carried out with D_2O and the ether layer collected, dried over molecular sieves and the ether removed to give only $C_6H_5CF{=}CFCH{=}CHCF_3$ and no $C_6H_5CF_2CFDCH{=}CHCF_3$ showing that the $[C_6H_5CF_2CFCH{=}CHCF_3]^-$ is not an intermediate.

Attempted Reaction of $CF_2{=}CFCH{=}CHCH_3$ with Diethylamine

A 250-ml, three-necked flask was equipped with a magetic stirrer, dropping funnel, reflux condenser, and thermometer. The ethyl ether (150 ml) and diethyl amine (7.4 grams) were placed in the flask and stirred at 5°C in an ice water bath before the diene $CF_2{=}CFCH{=}CHCH_3$ (12.2 grams, 0.1 mole) was added via the dropping funnel. There was no apparent reaction and the mixture was warmed to ambient temperature and stirred for 48 hours. The ethyl ether was then removed under vacuum to give 6.6 grams of higher boiling material which was distilled and determined to be the 2 + 2 cyclic dimer of the $CF_2{=}CFCH{=}CHCH_3$.

Reaction of $CF_2=CFCH_2CHBrCH_3$ with Magnesium

A 50-ml flask was equipped with a magnetic stirrer and a reflux condenser before being charged with magnesium turnings (0.1 mole, 2.4 grams) and 10 ml of ethyl ether. The $CF_2=CFCH_2CHBrCH_3$ (24 grams, 0.2 mole) was added and an immediate exotherm caused the ether to reflux. After the addition was complete, the mixture was hydrolyzed and the ether layer collected and dried over molecular sieves. The ether was removed to leave the starting material (13 grams) and higher boiling material (7 grams). Further vacuum distillation gave 1.1 grams of material identified as the desired coupled product along with polymeric material (Figure 79). Figure 79 - IR (liquid) maxima in microns 3.32 (C-H), 5.52 ($CF_2=CF$), 7.7, 7.95, 8.7, (C-F), 9.2, 12.5.

Attempted Reaction of $CF_2=CFCH=CHCF_3$ with H_2SO_4 and Water

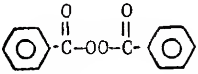
A 25-ml flask was equipped with a magnetic stirrer and a reflux condenser before being charged with water (10 ml) and H_2SO_4 (2 ml). The diene $CF_2=CFCH=CHCF_3$ (2 grams) was added and the mixture stirred for six hours. A sample was then taken and infrared analysis showed that no reaction had taken place.

SECTION 4

ENVIRONMENTAL IMPACT

Due to the small scale usage of chemicals and proper disposal procedures, there was no unexpected impact on the environment. A listing of the compounds used along with the (NIOSH) National Institute for Occupational Safety and Health Registry data are included.

1. Acetic acid (CH_3COOH) - AF-1225000 TXDS oral rat LD_{50}: 3310 mg/kg TL - 10 ppm DOT - corrosive material

2. Benzoyl peroxide  DM-8575000 TXDS oral-hum LDLo 500 mg/kg TL - 5 g/kg DOT - organic peroxide

3. Bromine (Br_2) EF - 9100000 TXDS inh mus LC_{50}: 750 ppm/ 9 min. TL - TWA 0.1 ppm DOT - corrosive material

4. Butadiene ($CH_2=CHCH=CH_2$) - EI-9275000 TXDS oral rat LD_{50}: 5480 mg/kg TL - 1000 ppm DOT - flammable gas

5. 1,2-Dibromo-2-chlorotrifluoroethane ($CF_2BrCFClBr$) KH-7600000 TXDS inh-rat LcLo 25,270 ppm/15 M harmless liquid for shipping purposes

6. Dichloroiodotrifluoroethane - No listing, considered harmless

7. Diethyleneglycol dimethyl ether ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) - No listing, considered nontoxic, compared to tetraethyleneglycol dimethyl ether.

8. Dimethyl sulfide (CH_3SCH_3) - PV-5075000 TXDS oral rat LD_{50}: 535 mg/kg DOT - flammable liquid

9. Dimethyl sulfoxide ($CH_3SO_2CH_3$) - PV-6210000 TXDS oral mus LD_{50}: 21 grams/kg DOT - flammable

10. Ethanol (CH_3CH_2OH) - KQ-6300000 TXDS oral rat LD_{50}: 14 grams/kg TL - 1000 ppm DOT - flammable liquid.

11. Ethylene ($CH_2=CH_2$) KU-5340000 TXDS inh mus LC_{50}: 95 ppm TLm 96: 1000-100 ppm DOT - flammable gas

12. Iodine (I_2) - NN-1575000 TXDS oral human LDLo: 5 mg/kg inh dog LDLo: 40 mg/kg TL - 0.1 ppm

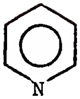
13. Methylene chloride (CH_2Cl_2) - PA-8050000 TXDS oral rat LD_{50}: 167 mg/kg TL - 2000 ppm DOT - ORM A otherwise restricted material

14. Ozone (Oz) - RS-8225000 TXDS inh rat LC_{50}: 4.8 ppm/4H TL - 0.1 ppm DOT - toxic gas

15. Potassium t-butoxide ($CH_3C(CH_3)_2O^-K^+$) - No listing DOT - corrosive solid.

16. Potassium hydroxide (KOH) - TT-2100000 TXDS oral rat LD_{50}: 365 mg/kg TL - 2 mg/m^3 DOT - corrosive material

17. Propene ($CH_2=CHCH_3$) UC-6740000 AQTX TLm 96: over 1000 ppm DOT - flammable gas

18. Pyridine  - UR-8400000 TXDS oral rat LD_{50}: 891 mg/kg TL - 5 ppm DOT - flammable liquid

19. Sodium hydroxide (NaOH) - WB-4900000 TL - 2 mg/m^3 IRDS skin rabbit 50 mg/24 H SEV DOT - corrosive material

20. Tetrafluoroethylene (CF_2=CF_2) - KX-4000000 TXDS inh rat LC_{50}: 40,000 ppm/4 H DOT - Flammable gas

21. Trifluoropropene (CF_3CH=CH_2) - No listing

22. Zinc (Zn) - ZG-8600000 TXDS inh human TCLo: 124 mg/m^3/ 50 min.

23. Zinc bromide ($ZnBr_2$) - ZN 1400000 TXDS oral rat LD_{50}: 350 mg/kg TL 1 mg/m^3 DOT - corrosive solid

Explanation of Symbols and Abbreviations for Environmental Impact

TXDS	Toxic dose data
inh	Inhalation
rat	rat
ppm	Parts per million
M	Minutes (min.)
LcLo	Lowest lethal concentration
LD_{50}	Lethal dose calculated to cause 50% of the experimental animal population to die
LDLo	Lowest lethal dose
TL	Threshold limits
TLm 96	Concentration which will kill 50% of the exposed organism within 96 hours
AQTX	Aquatic toxicity ratings
SEV	Severe irritation effects
DOT	Department of Transportation

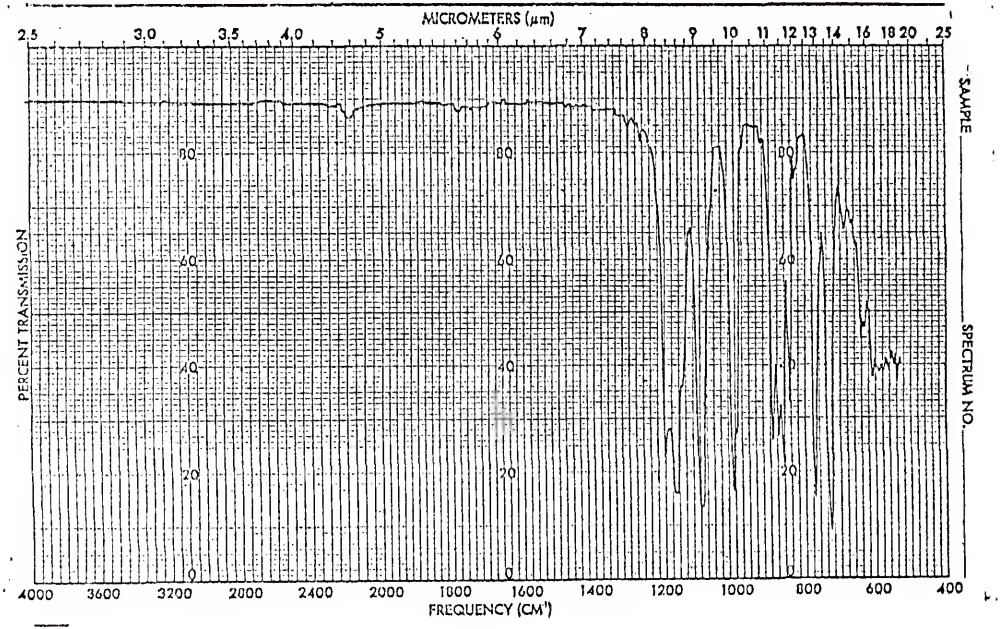


Figure 1 - Infrared Spectrum of $CF_2BrCFClBr$

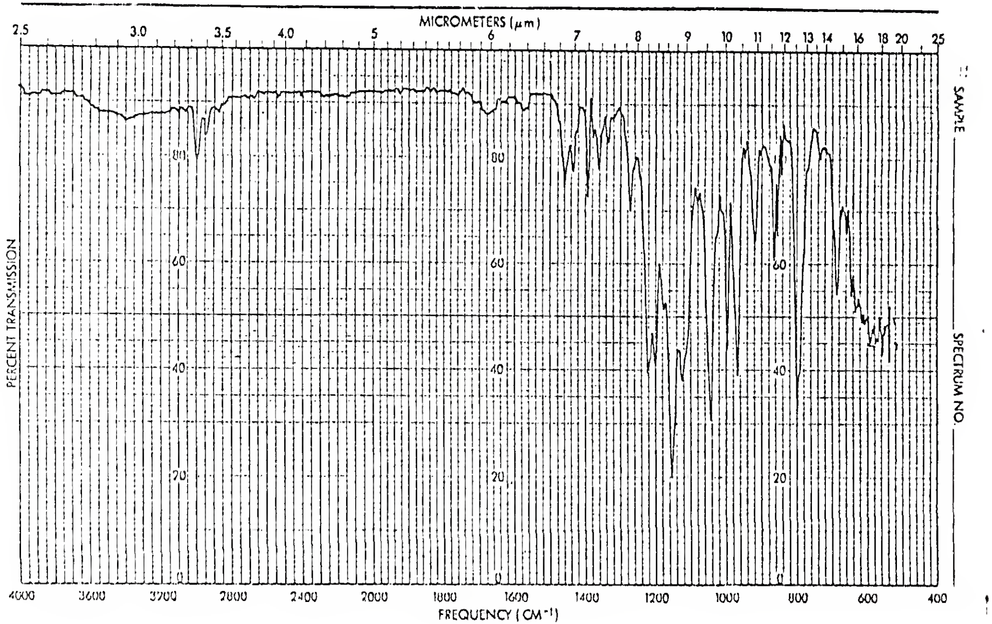


Figure 2 - Infrared Spectrum of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ Lower Boiling Diastereomer

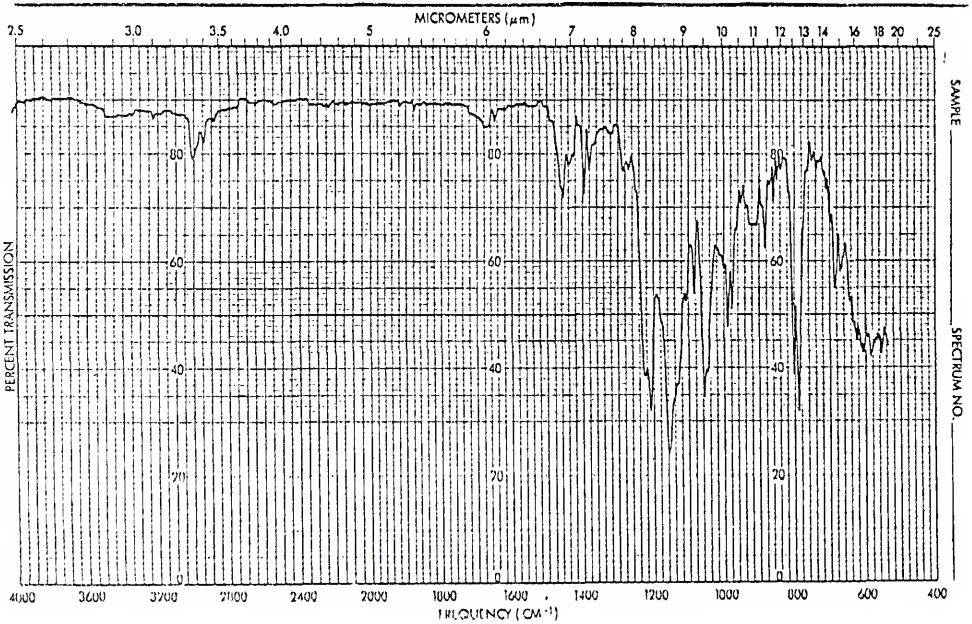


Figure 3 - Infrared Spectrum of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ Higher Boiling Diastereomer

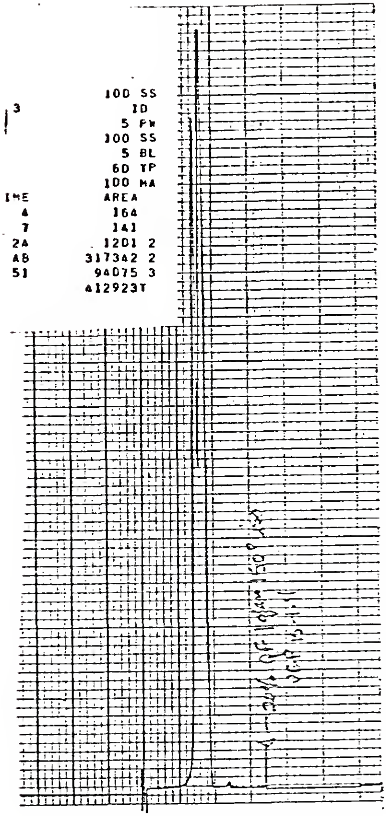


Figure 4 - GLC of Mid-cut from Distillation of the Two Diastereomers of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$

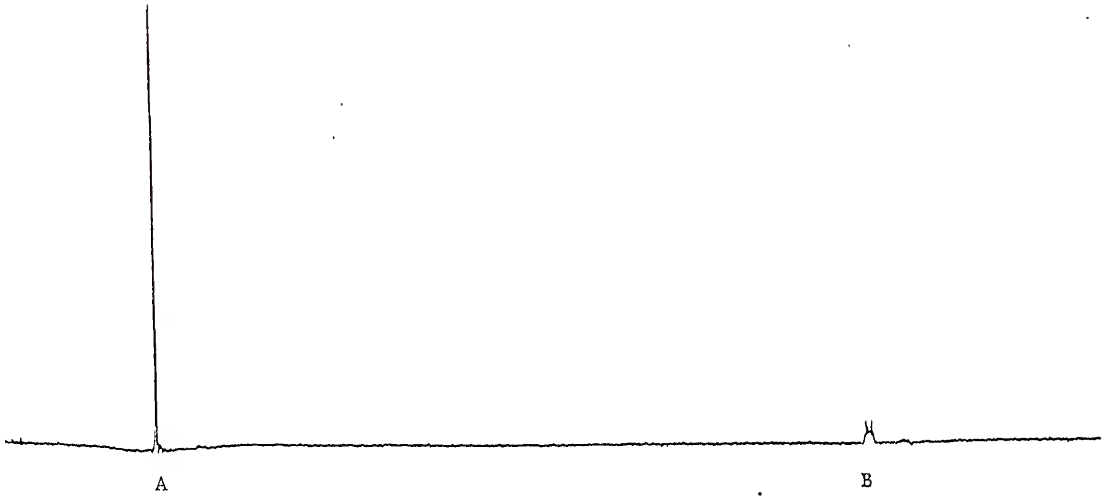


Figure 5 - F^{19} NMR of Lower Boiling Diastereomer of $\underset{A}{CF_2}Br\underset{B}{\overset{*}{C}}FClCH_2\overset{*}{C}HBrCH_3$

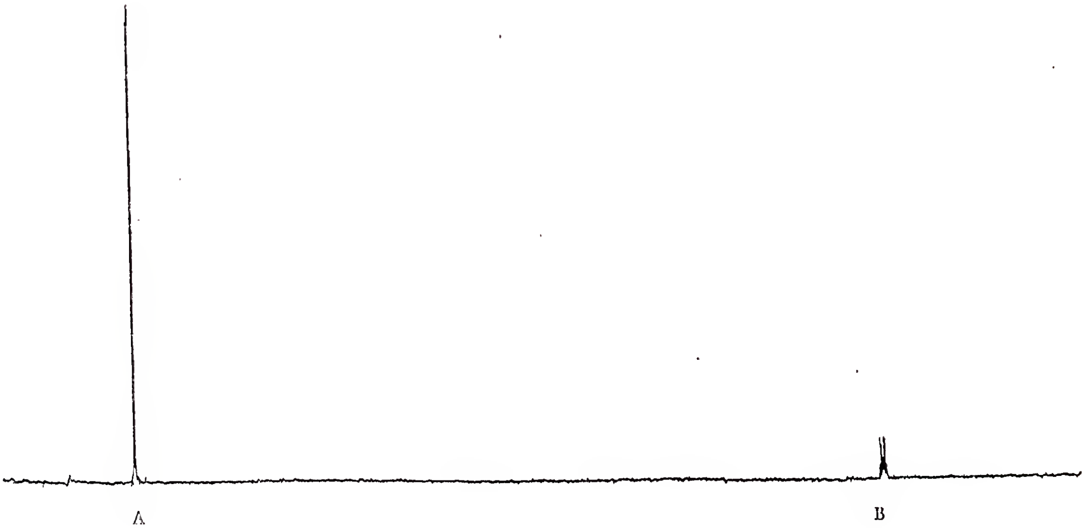
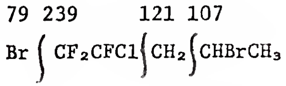


figure 6 - F^{19} NMR of Higher Boiling Diastereomer of $\underset{A}{CF_2}Br\underset{B}{\overset{*}{C}F}ClCH_2\overset{*}{C}HBrCH_3$

TABLE XI

MASS SPECTRUM OF $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}HBrCH_3$ (BOTH DIASTEREOMERS)

Molecular Weight 320. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$\overset{79}{Br}\Big(\overset{239}{CF_2CFCl}\Big(\overset{121}{CH_2}\Big(\overset{107}{CHBrCH_3}$$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
320	0.2 $M^{\oplus}$	118	1.6
318	0.4	116	4.2
316	0.2	113	6.0
241	6.5	111	16.3
240	1.5	110	1.7
239	26.4	109	61.9
238	1.3	108	3.7
237	20.6	107	69.5
219	1.2	106	1.4
217	1.1	105	1.1
204	1.4	103	2.5
203	21.1	102	4.0
202	1.5	101	9.7
201	22.0	96	1.0
197	1.4	95	26.8
195	1.0	94	1.2
183	4.0	93	19.8
181	4.1	91	3.0
175	1.4	89	1.6
173	2.0	87	3.0
171	1.3	85	5.5
160	1.1	83	2.8
159	14.9	82	3.6
158	3.1	81	3.9
157	53.6	80	4.6
155	9.1	79	4.3
153	1.3	78	2.0
147	2.3	77	13.1
145	2.0	76	1.1
142	1.0	75	10.2
141	1.1	73	3.0
140	1.0	72	3.5
139	11.0	71	7.8
138	2.4	70	1.9
137	20.2	69	15.4
131	6.2	68	1.6
129	7.5	67	3.0
127	1.5	66	2.0
123	3.8	65	35.7
122	11.1	64	3.3
121	26.5	63	100.0
120	1.3	62	1.3
119	3.4	61	3.2

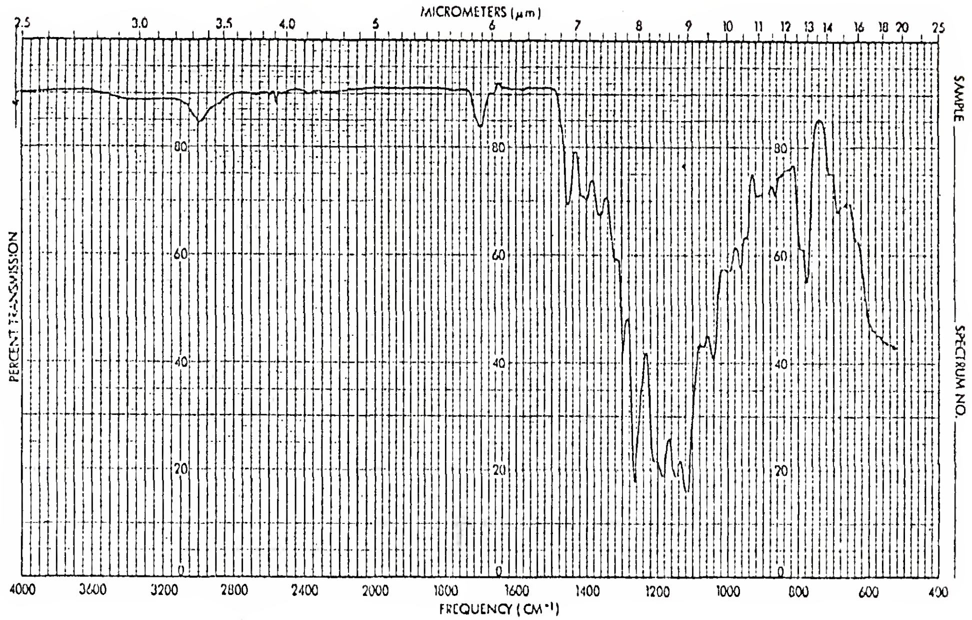


Figure 7 - Infrared of $CF_2Br\overset{*}{C}FClCH_2\overset{*}{C}H(CF_3)CH_2\overset{*}{C}HBrCF_3$

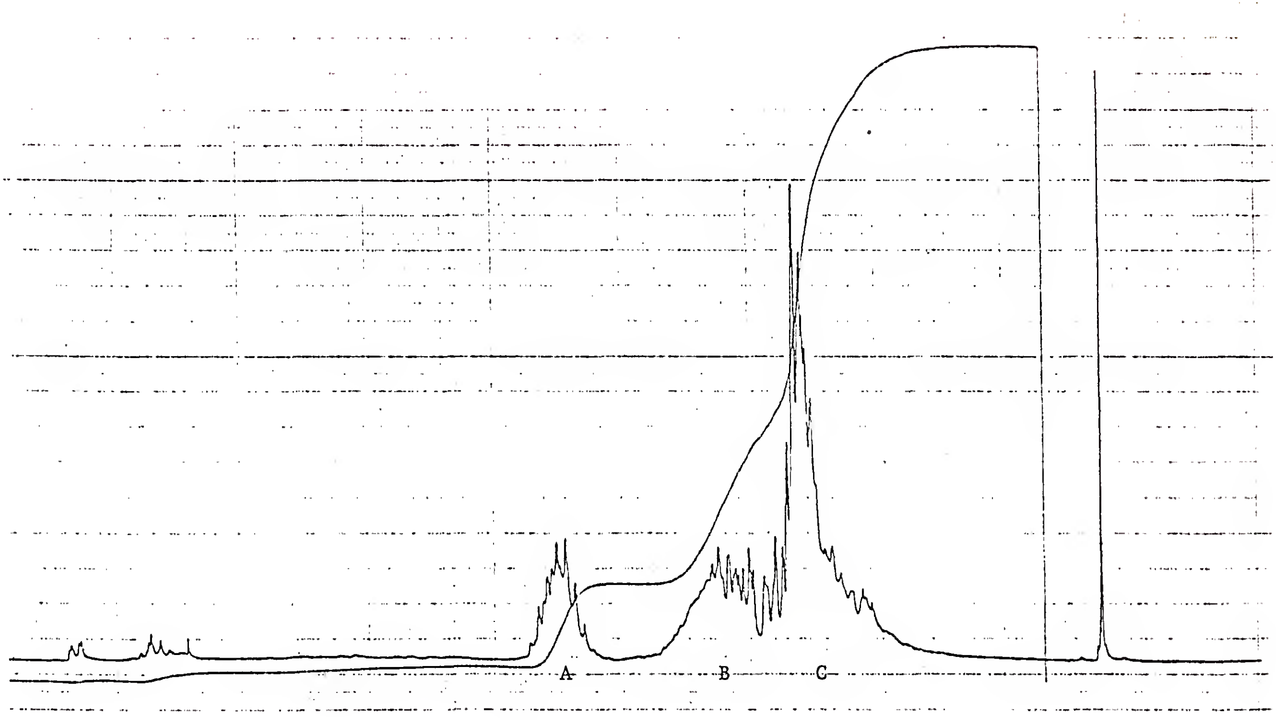


Figure 8 - H^1 NMR of $CF_2Br\underset{C}{\overset{*}{C}}FCl\underset{B}{C}H_2\underset{C}{\overset{CF_3}{C}}HCH_2\underset{A}{\overset{*}{C}}HBrCF_3$

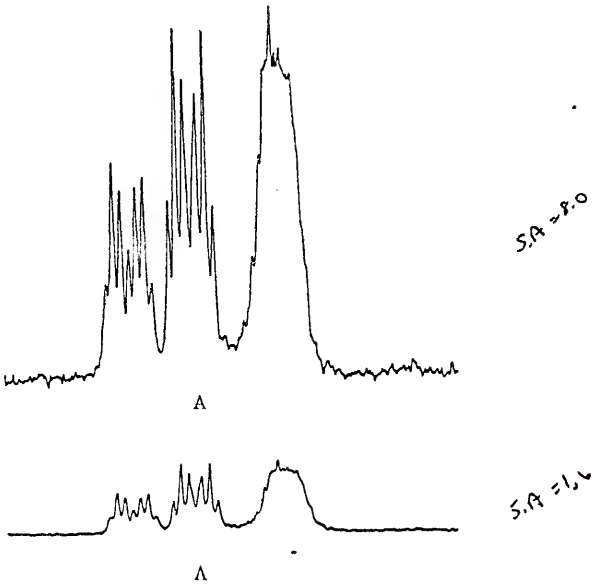


Figure 9 - F^{19} NMR of $CF_2Br\overset{*}{\underset{A}{C}}FClCH_2\overset{*}{\underset{\overset{|}{CF_3}}{C}}HCH_2\overset{*}{C}HBrCF_3$

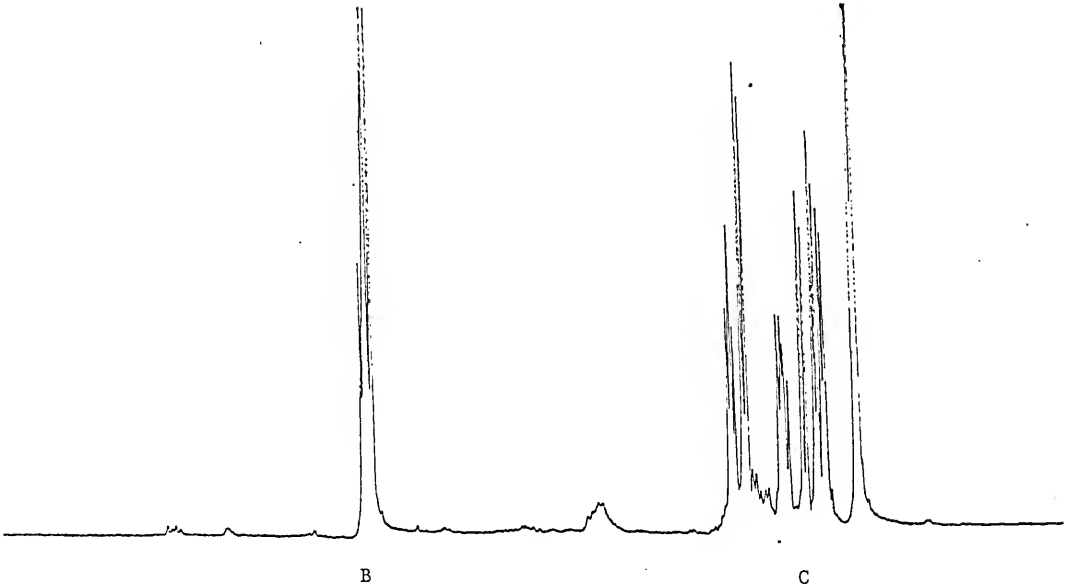
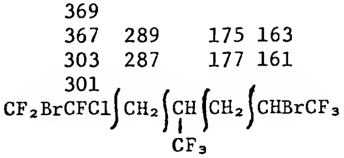


Figure 10 - F^{19} NMR of $\underset{B}{CF_2}Br\overset{*}{C}FClCH_2\underset{\underset{C}{CF_3}}{\overset{*}{C}}HCH_2\overset{*}{C}HBr\underset{C}{CF_3}$

TABLE XII

MASS SPECTRUM OF $\mathrm{CF_2\overset{*}{Br}CFClCH_2\underset{CF_3}{\overset{*}{C}}HCH_2\overset{*}{C}HBrCF_3}$

Molecular Weight 445. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$\mathrm{CF_2BrCFCl}\overset{369,\,367,\,303,\,301}{\Big|}\mathrm{CH_2}\overset{289,\,287}{\Big|}\underset{\mathrm{CF_3}}{\mathrm{CH}}\overset{175,\,177}{\Big|}\mathrm{CH_2}\overset{163,\,161}{\Big|}\mathrm{CHBrCF_3}$$

Nominal Mass	% Int. Base
445	1.7 $M^{\oplus}$
443	1.2
391	1.2
389	3.8
388	1.1
387	3.1
383	1.2
371	4.1
370	2.0
369	18.0
368	1.7
367	14.9
354	1.6
353	17.3
351	19.5
349	14.1
347	10.9
341	2.1
339	8.2
337	6.2
334	1.2
333	13.3
330.5	14.5
327	1.2
321	1.5
319	5.4
317	4.1
313	1.3
311	1.1
309	2.0
307	5.7
305	3.3
303	5.4
301	2.9
299	1.4
297	1.0
289	9.2
288	2.5
287	26.1
285	3.3
283	1.4
273	2.3
272	3.8
271	34.8
269	5.5
268	2.3
267	5.5
265	1.5
264	1.0
263	1.3
259	3.9
258	1.5
257	11.8
255	2.4
253	6.3
252	5.2
251	37.9
249	1.7
[Peaks >5%]	
237	6.0
232.5	5.1
225	9.5

Nominal Mass	% Int. Base
223	5.4
221	9.7
211	5.7
209	7.0
207	6.2
205	5.1
201	12.1
195	6.8
193	9.0
191	8.9
189	10.3
183	5.9
179	5.6
177	44.1
176	7.5
175	41.6
173	5.5
171	11.7
163	13.4
161	12.0
157	11.9
155	6.1
147	5.1
145	19.1
143	6.7
139	5.6
133	9.3
131	23.9
129	22.4
127	25.7
126	5.8
121	5.0
116	8.0
115	8.4
113	42.5
111	33.1
109	14.3
108	7.3
101	6.2
96	5.7
95	100.0
93	7.5
89	8.0
85	23.0
82	6.1
80	7.5
77	72.0
75	11.5
69	67.3
67	12.7

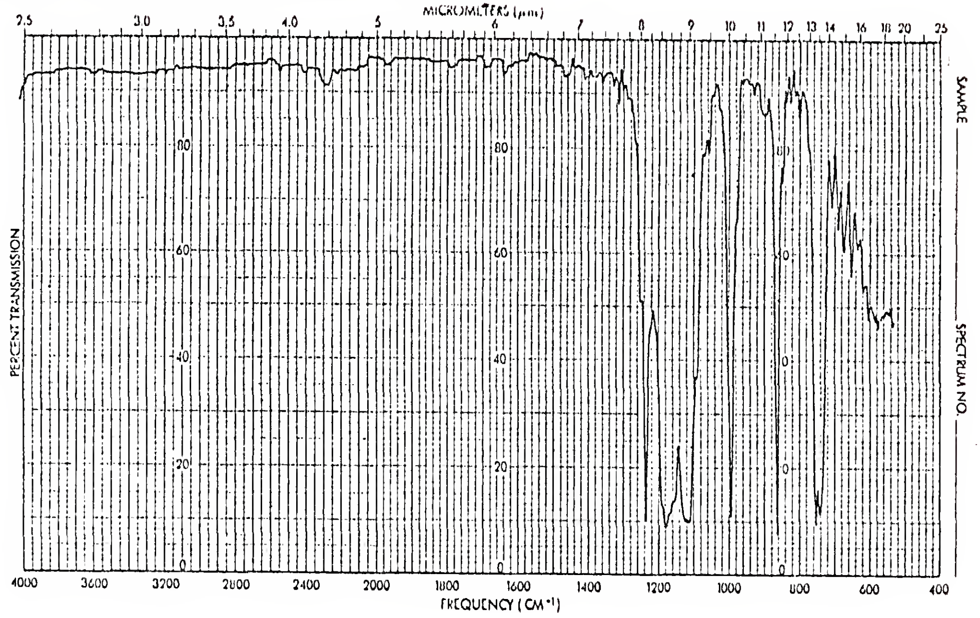


Figure 11 - Infrared Spectrum of CF_2BrCF_2I

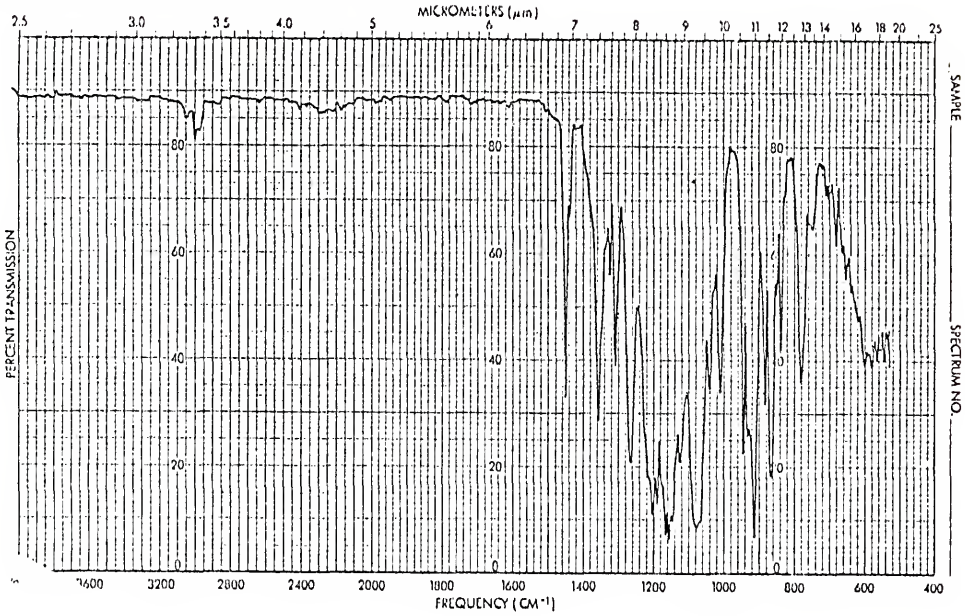


Figure 12 - Infrared Spectrum of $CF_2BrCF_2CH_2CH_2I$

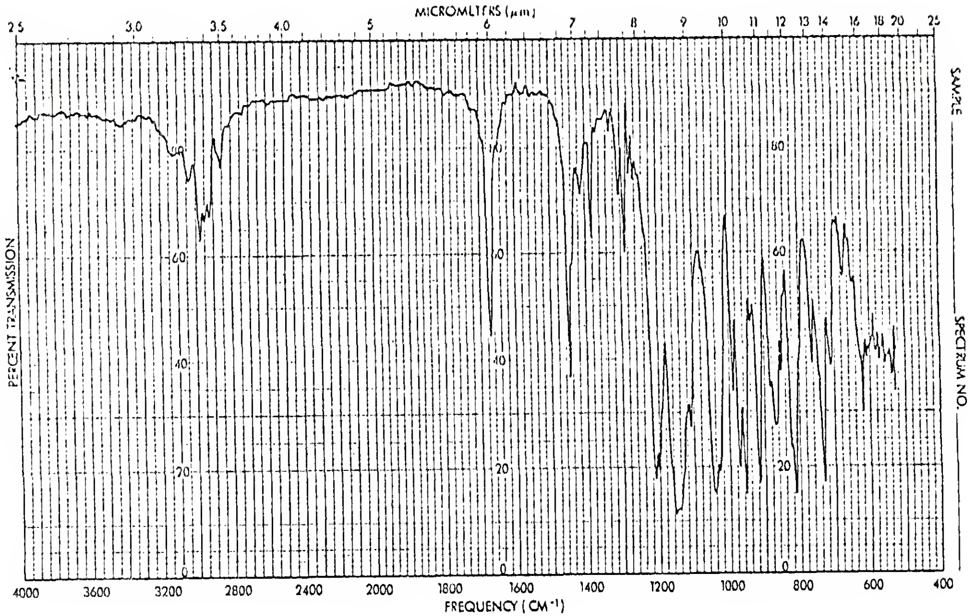


Figure 13 - Infrared of $CF_2BrCFClCH=CHCH_3$

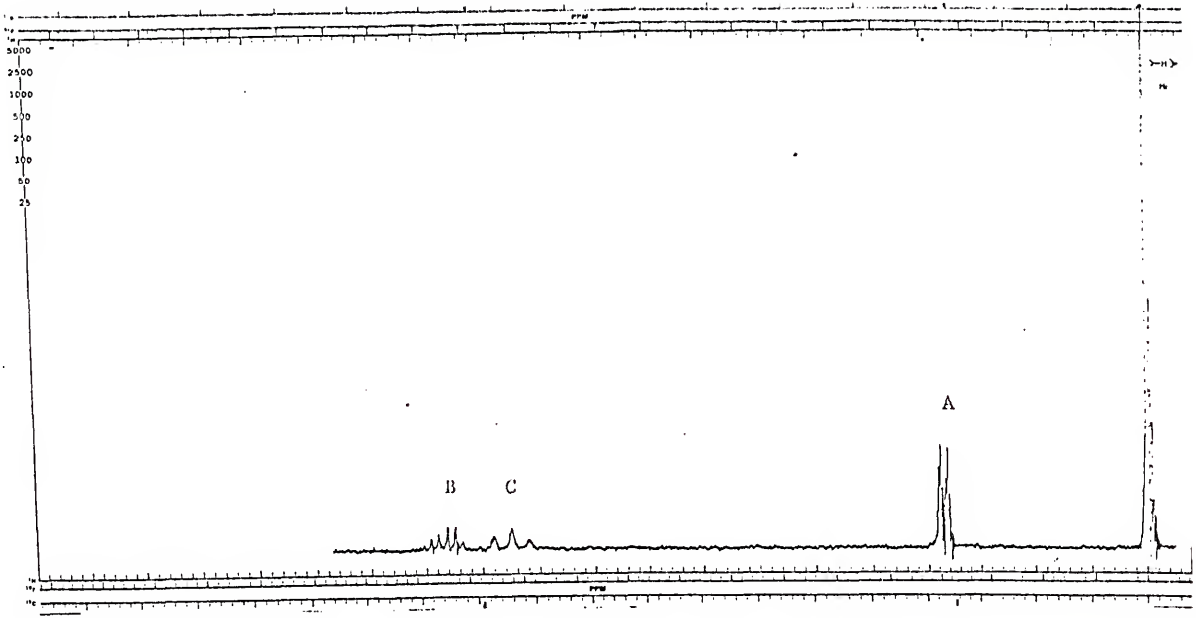


Figure 14 - H^1 NMR of $CF_2Br\overset{*}{C}FClCH=CHCH_3$
C B A

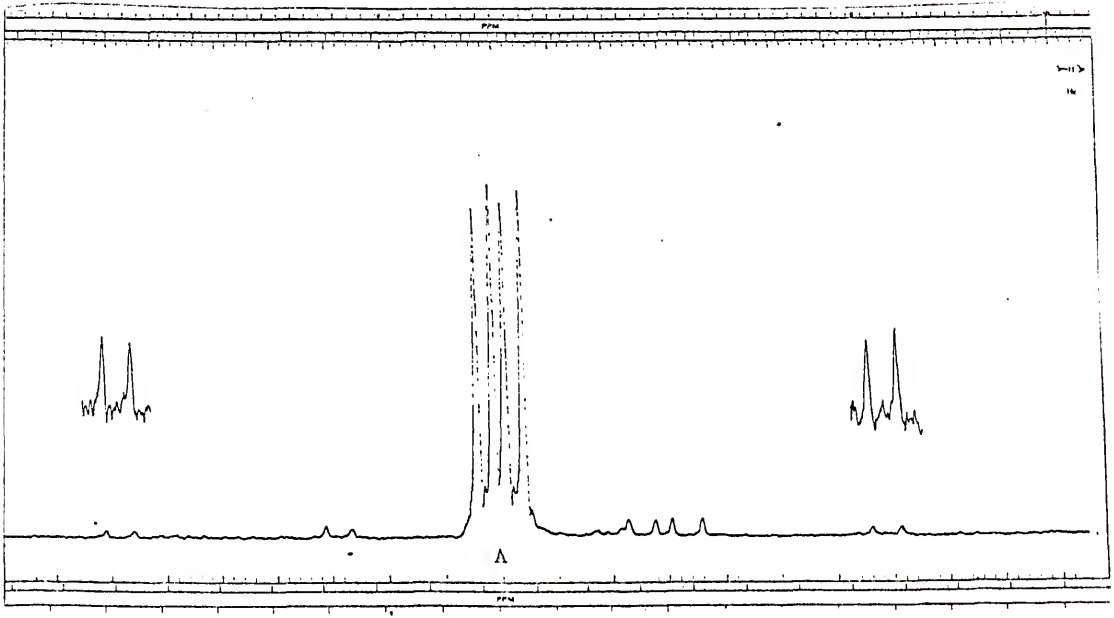
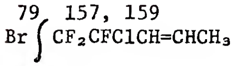


Figure 15 - F^{19} NMR of $\underset{A}{CF_2}Br\overset{*}{C}FClCH{=}CHCH_3$

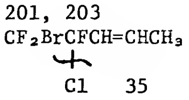
TABLE XIII

MASS SPECTRUM OF $CF_2Br\overset{*}{C}FClCH=CHCH_3$

Molecular Weight 238. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.

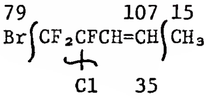


$\overset{79}{Br}\,\Big|\,\overset{157,\ 159}{CF_2CFClCH=CHCH_3}$



$\overset{201,\ 203}{CF_2Br\underset{\underset{Cl\quad 35}{\mid}}{C}FCH=CHCH_3}$

Base peak 107



$\overset{79}{Br}\,\Big|\,\overset{107}{CF_2\underset{\underset{Cl\quad 35}{\mid}}{C}FCH=CH}\,\Big|\,\overset{15}{CH_3}$

Nominal Mass	%Int. Base	Nominal Mass	% Int. Base
238	0.7 $M^{\oplus}$	91	4.6
236	0.6	89	2.3
203	4.4	87	5.4
201	4.6	85	2.1
159	2.0	82	1.7
157	6.8	81	2.2
139	1.9	80	1.9
138	1.6	79	1.4
137	4.1	77	4.4
131	1.9	75	5.5
129	2.4	73	1.0
122	9.5	72	6.1
121	8.6	71	24.5
119	1.1	70	2.2
111	2.4	69	7.0
110	1.6	68	1.3
109	32.5	67	1.7
108	4.7	63	1.7
107	100.0	61	2.6
106	1.0	60	1.0
103	1.6	59	3.6
102	3.1	57	4.7
101	9.3	56	1.8
95	9.0	51	20.4
93	3.9		

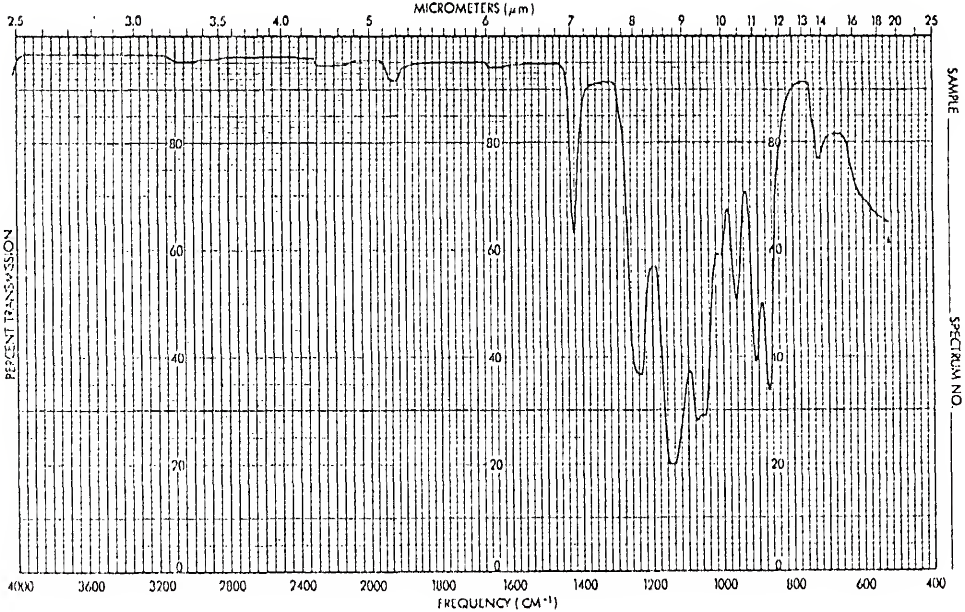


Figure 16 - Infrared Spectrum of $CF_2BrCF_2CH=CH_2$

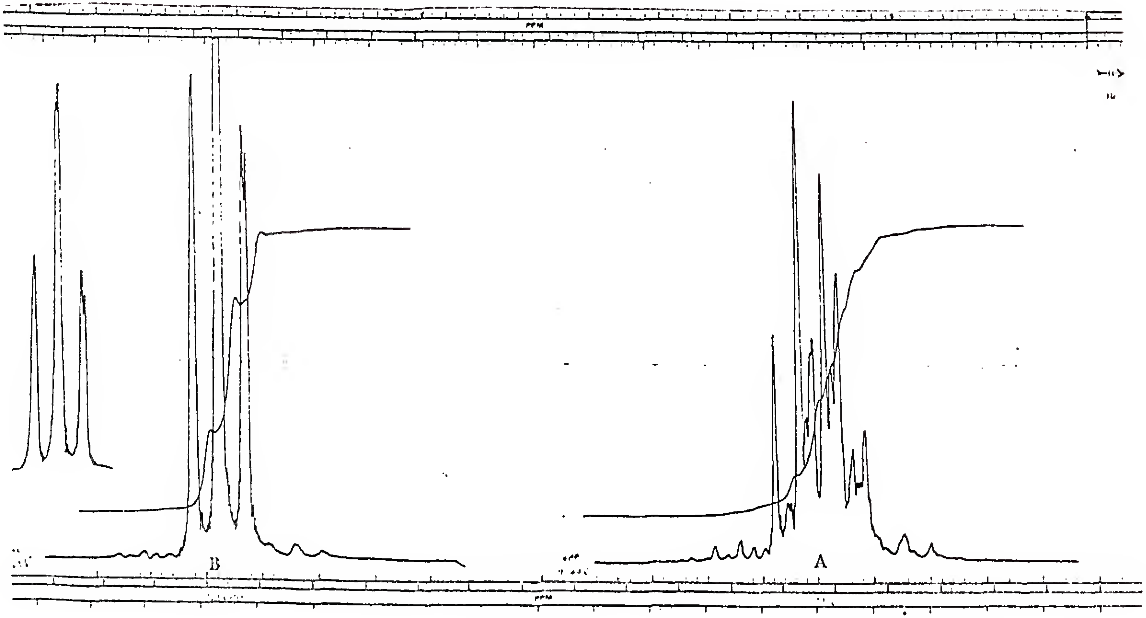
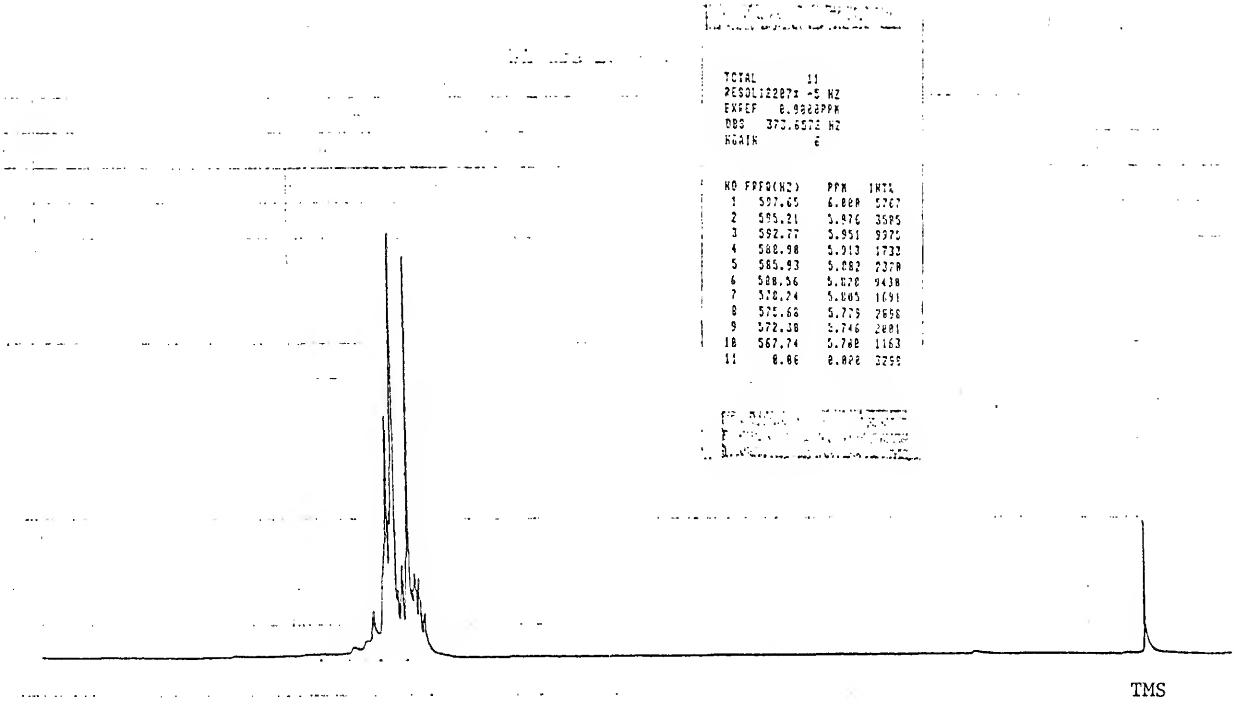


Figure 17 - F^{19} NMR of $\underset{B}{CF_2Br}\underset{A}{CF_2}CH=CH_2$



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TOTAL          11
RESOL:22087x -5 HZ
EXREF    0.9922PPM
OBS   373.6572 HZ
HGAIN          6

NO FREQ(HZ)    PPM   INTL
 1   597.65    6.008  5767
 2   595.21    5.976  3585
 3   592.77    5.951  9975
 4   588.98    5.913  1733
 5   585.93    5.882  2378
 6   580.56    5.828  9438
 7   578.24    5.805  1691
 8   575.68    5.779  2656
 9   572.38    5.746  2081
10   567.74    5.700  1163
11     0.00    0.000  3299
```

Figure 18 - H^1 NMR of $CF_2BrCF_2CH=CH_2$

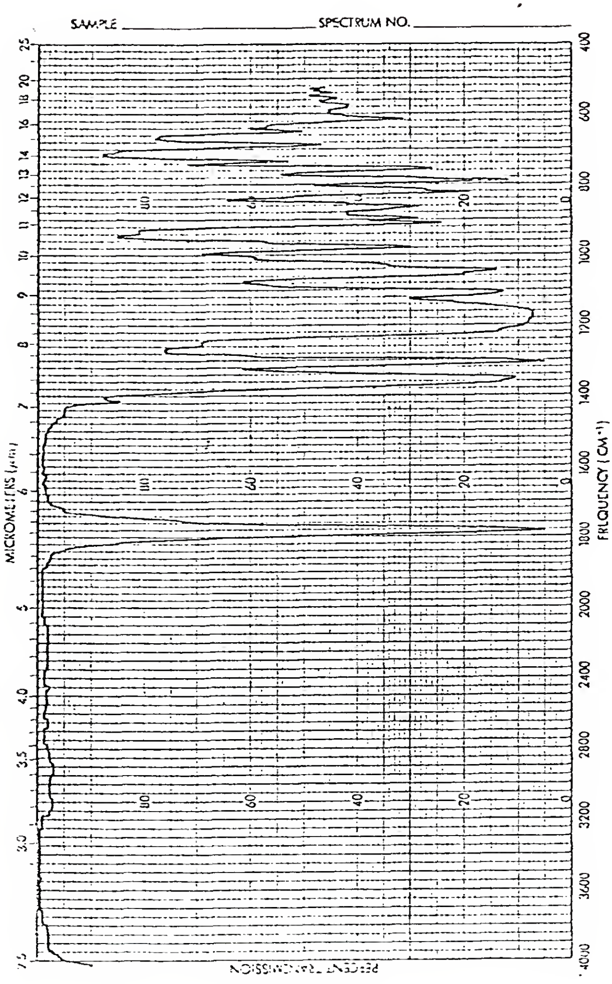

Figure 19 - Infrared Spectrum of $CF_2ClCFBrCF_2CF=CF_2$

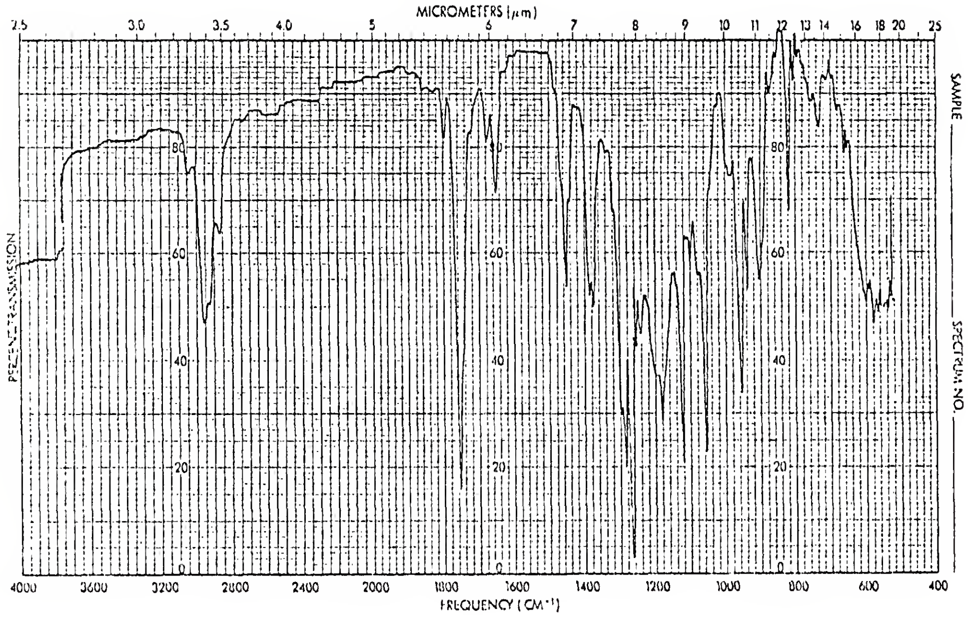

Figure 20 - Infrared Spectrum of $CF_2=CFCH=CHCH_3$

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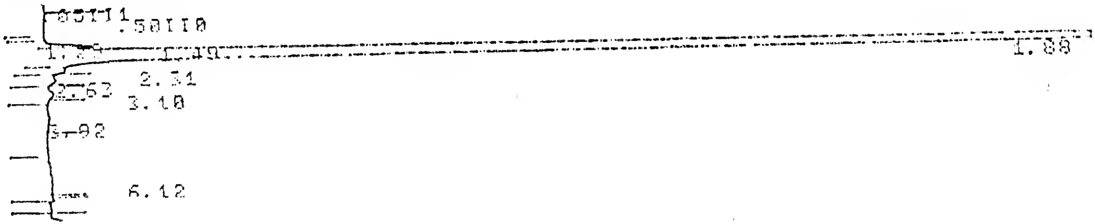

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IGP-22-1
                      COLUMN:GLASS 20% QF-1
   L TEMP:  30          HELD FOR:  2 MIN
   TEMP: 200

'EAK#      AREA%        RT        AREA BC

  1         0.041      1.29        320 02
  2         1.292      1.49      10132 02
  3        97.19       1.88     762267 08
  4         0.137      2.31       1075 05
  5         0.159      2.63       1246 05
  6         0.249      3.1        1951 01
  7         0.077      3.92        600 21
  8         0.857      6.12       6719 21

TOTAL      100.                 784310
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Figure 21 - GLC Analysis of $CF_2=CFCH=CHCH_3$

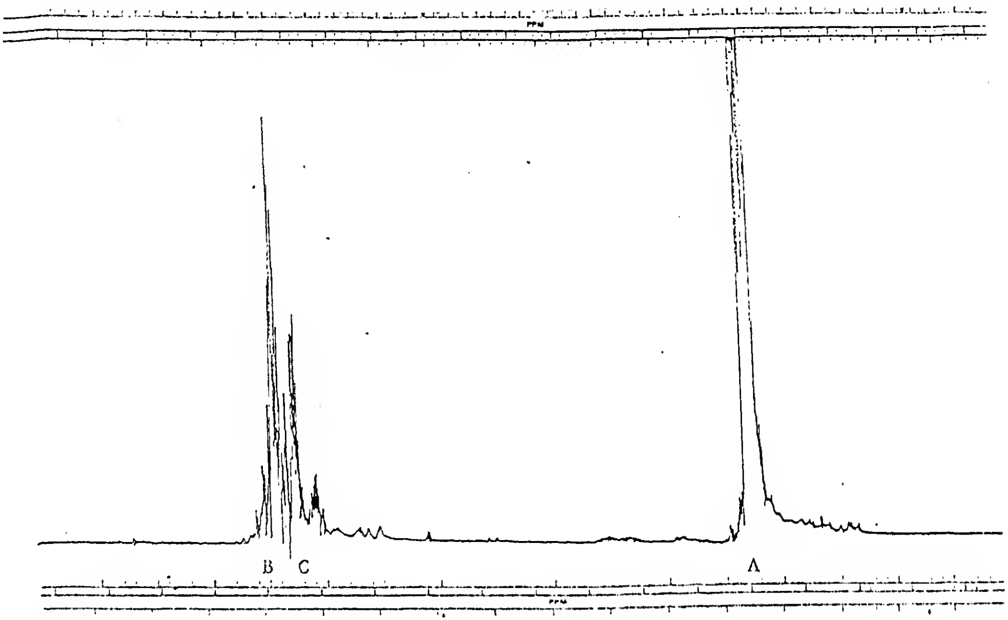


Figure 22 - H^1 NMR of CF_2=CFCH=CHCH$_3$
C B A

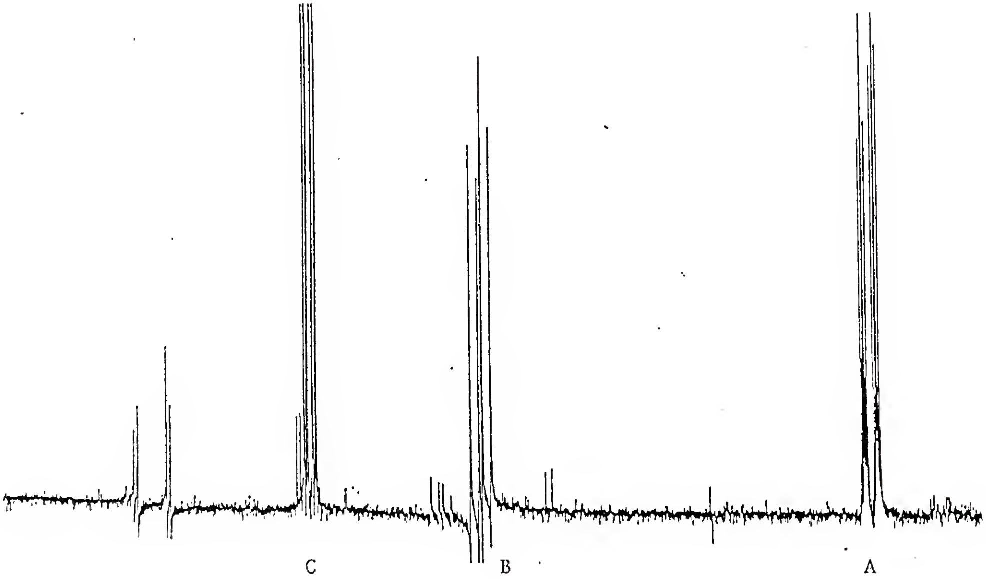


Figure 23 - F^{19} NMR of

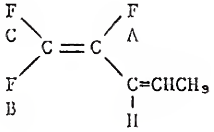
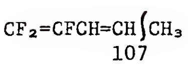


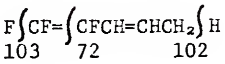
TABLE XIV

MASS SPECTRUM OF $CF_2{=}CFCH{=}CHCH_3$

Molecular Weight 122. Listing of all peaks with >1% base intensity along with $M^{\oplus}$ peak.



$CF_2{=}CFCH{=}CH\underset{107}{\int}CH_3$



$\underset{103}{F}\int CF{=}\underset{72}{\int}CFCH{=}CHCH_2\underset{102}{\int}H$

Nominal Mass	% Base Int.	Nominal Mass	% Base Int.
122	100.0 $M^{\oplus}$		>5% Base Intensity
121	25.3	89	5.6
120	2.8	83	10.8
119	5.4	77	23.0
111	1.4	76	7.2
107	4.4	75	24.6
106	2.4	72	49.1
104	1.4	71	27.3
103	19.7	70	11.0
102	12.2	69	32.2
101	47.3	58	5.5
100	1.1	57	25.1
99	3.5	56	5.9
96	2.0	53	27.3
95	32.7	52	8.2
94	3.6	51	39.5
93	2.4	50	13.3

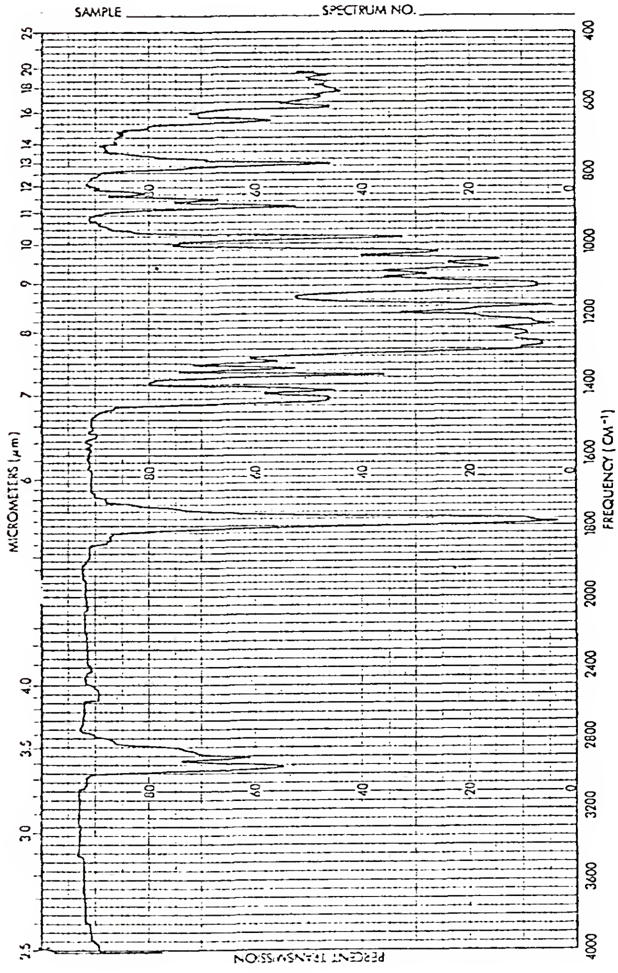


Figure 24 - Infrared Spectrum of $CF_2=CFCH_2CHBrCH_3$

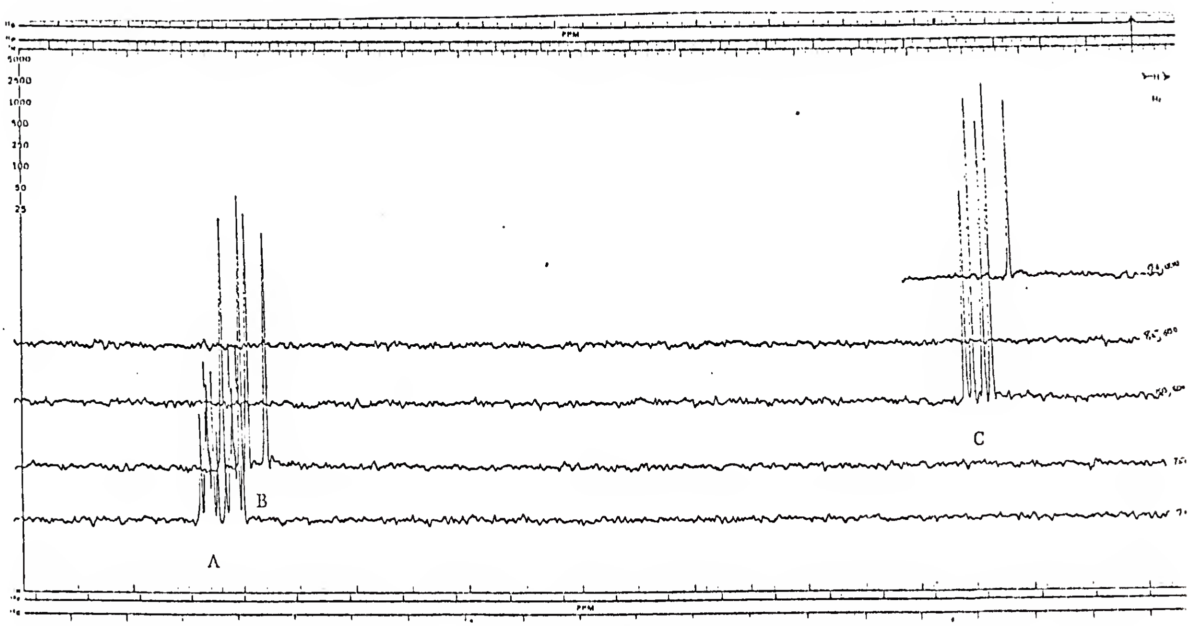
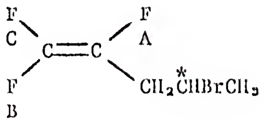


Figure 25 - F^{19} NMR of



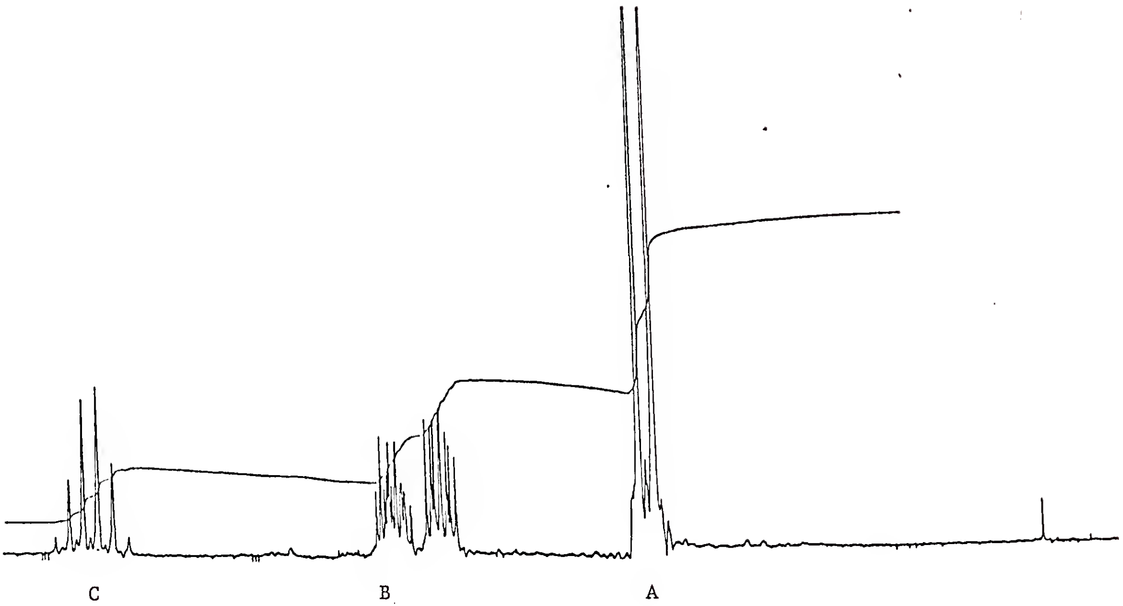
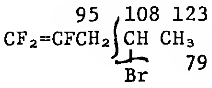


Figure 26 - H^1 NMR of $CF_2{=}CFCH_2\overset{*}{C}HBrCH_3$
B C A

TABLE XV

MASS SPECTRUM OF $CF_2{=}CFCH_2CHBrCH_3$

Molecular Weight 204. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$\overset{95}{CF_2{=}CFCH_2}\,\overset{108}{\underset{\underset{79}{Br}}{CH}}\,\overset{123}{CH_3}$$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
204	9.8 $M^{\oplus}$	94	1.2
202	10.1	93	1.5
157	1.3	89	2.4
155	1.3	88	1.5
124	5.8	86.5	2.6
123	100.0	84	1.1
122	6.9	83	5.6
121	2.7	82	4.5
110	1.3	81	2.8
109	50.0	[Peaks >5% Int. base]	
108	8.5	77	21.8
107	48.7	75	9.6
106	2.0	73	9.0
104	3.3	72	7.9
103	16.6	69	44.3
102	1.5	59	67.9
101	4.6	57	12.7
96	4.6	53	9.5
95	56.4	51	18.3

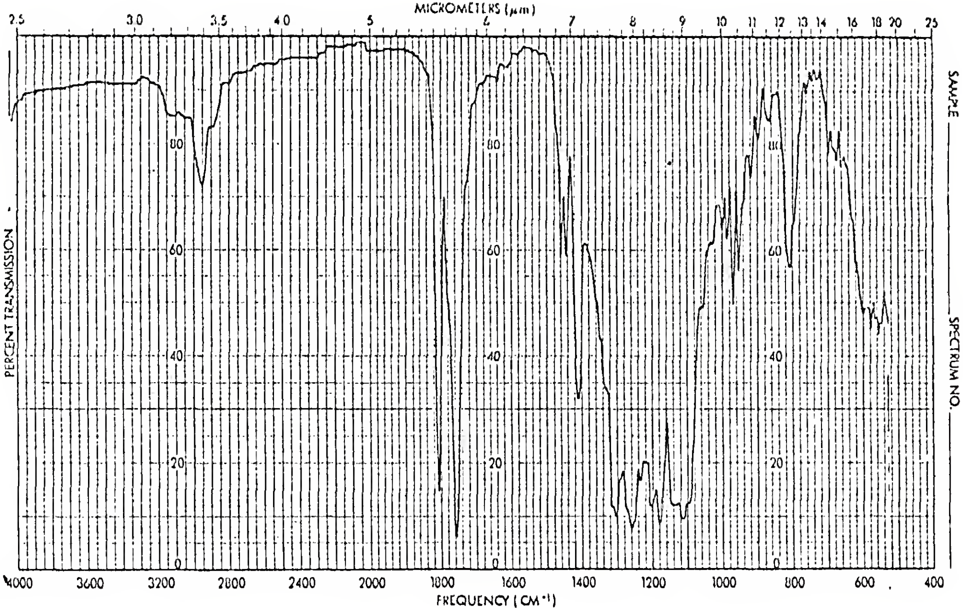


Figure 27 - Infrared Spectrum of $CF_2{=}CF\underset{\underset{\displaystyle CF_3}{|}}{CH_2CH}CH_2CH{=}CF_2$

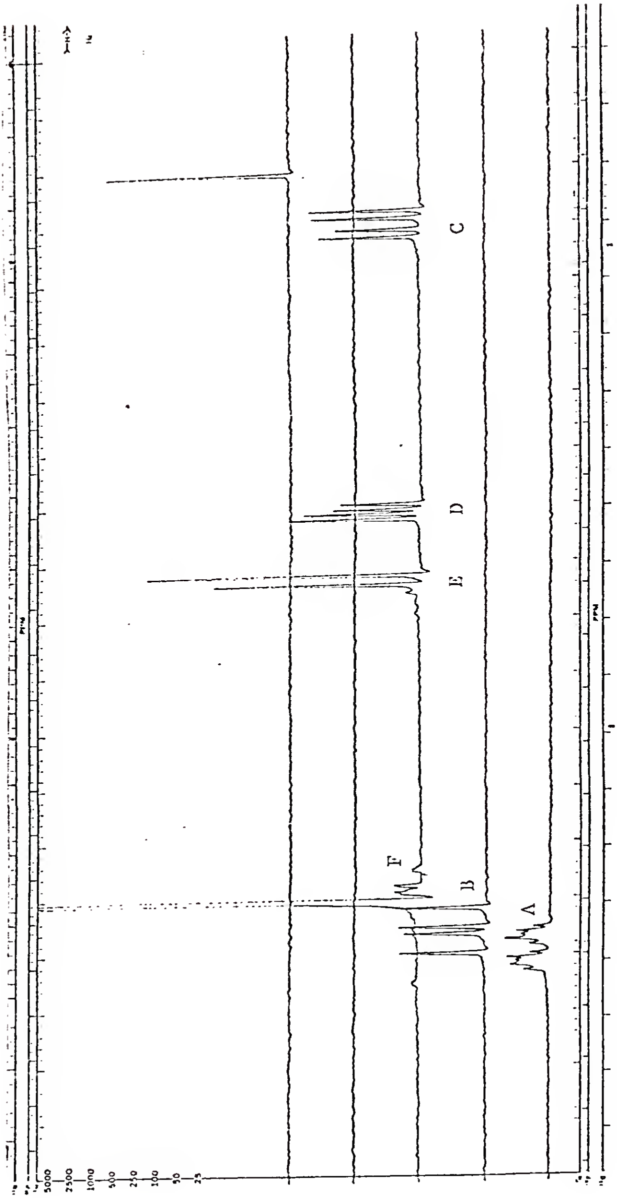
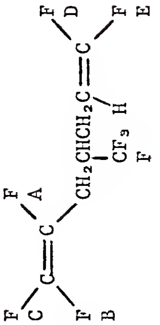


Figure 28 - F^{19} NMR of



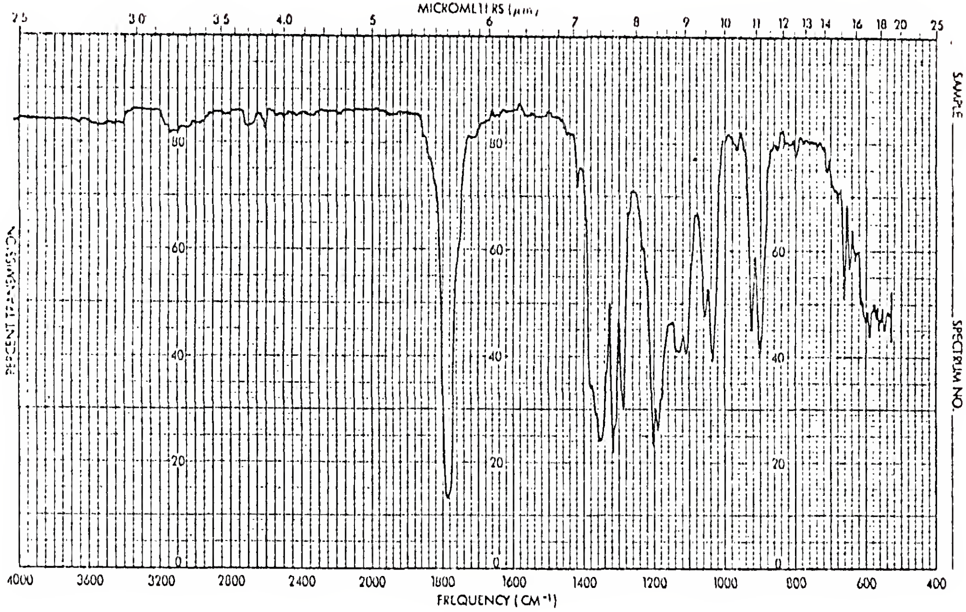


Figure 29 - Infrared Spectrum of $CF_2{=}CFCF_2CF{=}CF_2$

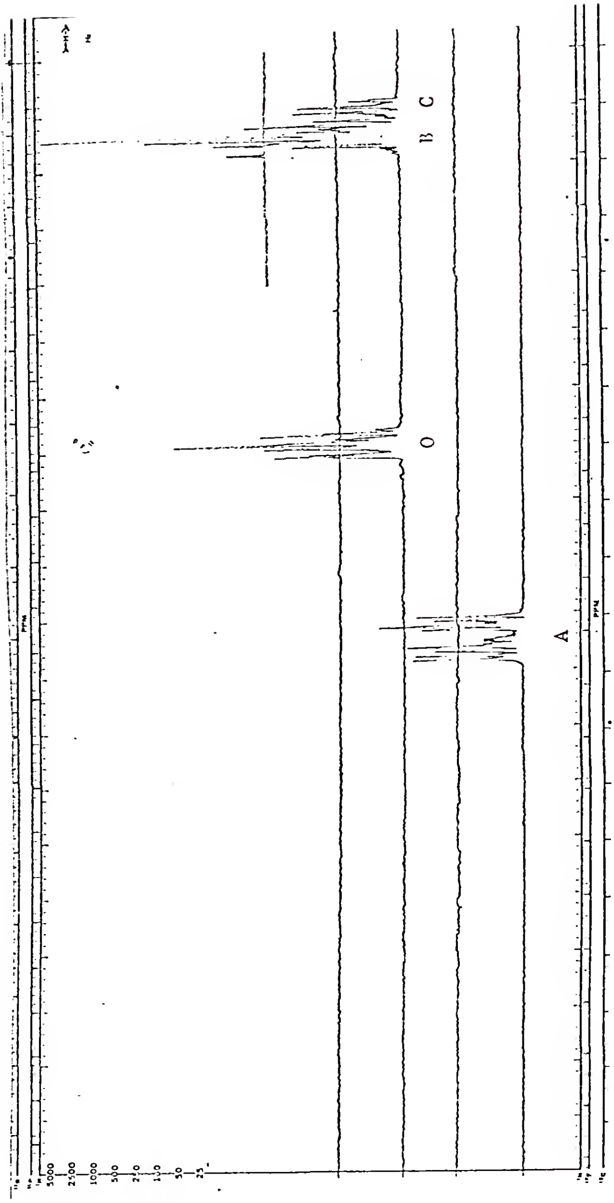
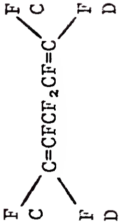


Figure 30 - F^{19} NMR of

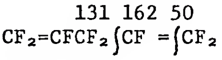


$$\begin{array}{c}F_C\\F_D\end{array}C{=}CFCF_2CF{=}C\begin{array}{c}F_C\\F_D\end{array}$$

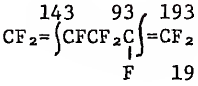
TABLE XVI

MASS SPECTRUM OF $CF_2{=}CFCF_2CF{=}CF_2$

Molecular Weight 212. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$\begin{array}{l} \qquad\qquad 131\ \ 162\ \ 50 \\ CF_2{=}CFCF_2\int CF = \int CF_2 \end{array}$$



$$\begin{array}{l} \qquad\quad 143 \quad\ 93\ \ 193 \\ CF_2{=}\int CFCF_2\underset{|}{C}\int{=}CF_2 \\ \qquad\qquad\quad\ F \quad 19 \end{array}$$

Nominal Mass		% Int. Base
213		2.9
212	$M^{\oplus}$	52.7
205		1.4
195		1.2
194		16.4
163		1.6
162		36.5
155		1.7
144		4.7
143		84.3
132		3.2
131		100.0
124		12.1
117		1.3
112		9.7
105		3.7
100		1.6
94		3.0
93		87.7
86		1.9
85		1.0
81		5.4
75		2.3
74		13.6
69		57.1
62		3.5
55		6.3
50		5.0
43		1.0
32		9.1
31		54.8
29		1.3
28		29.7

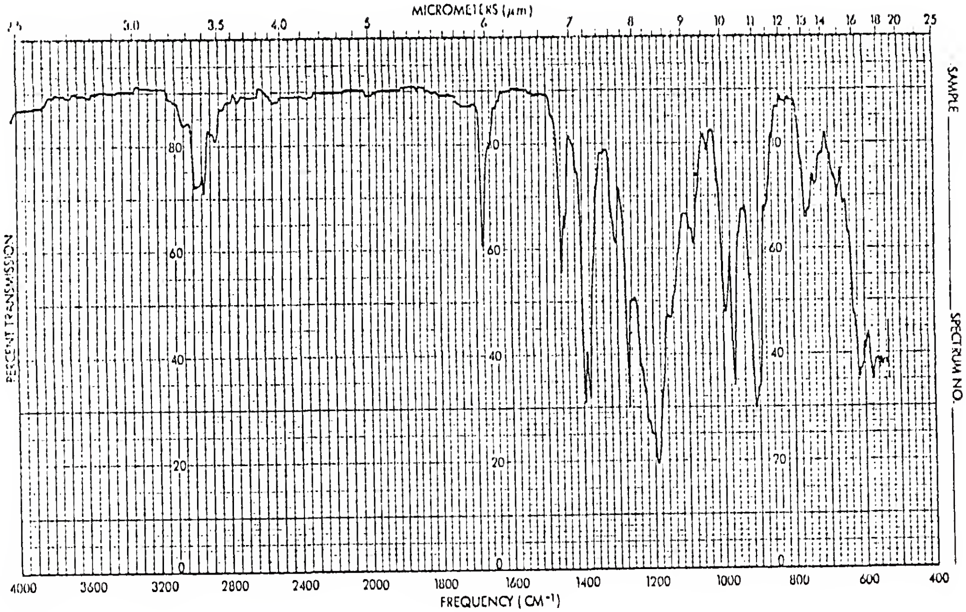


Figure 31 - Infrared Spectrum of $\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ | \quad\;\; | \\ CF_2CFCH{=}CHCH_3 \end{array}$

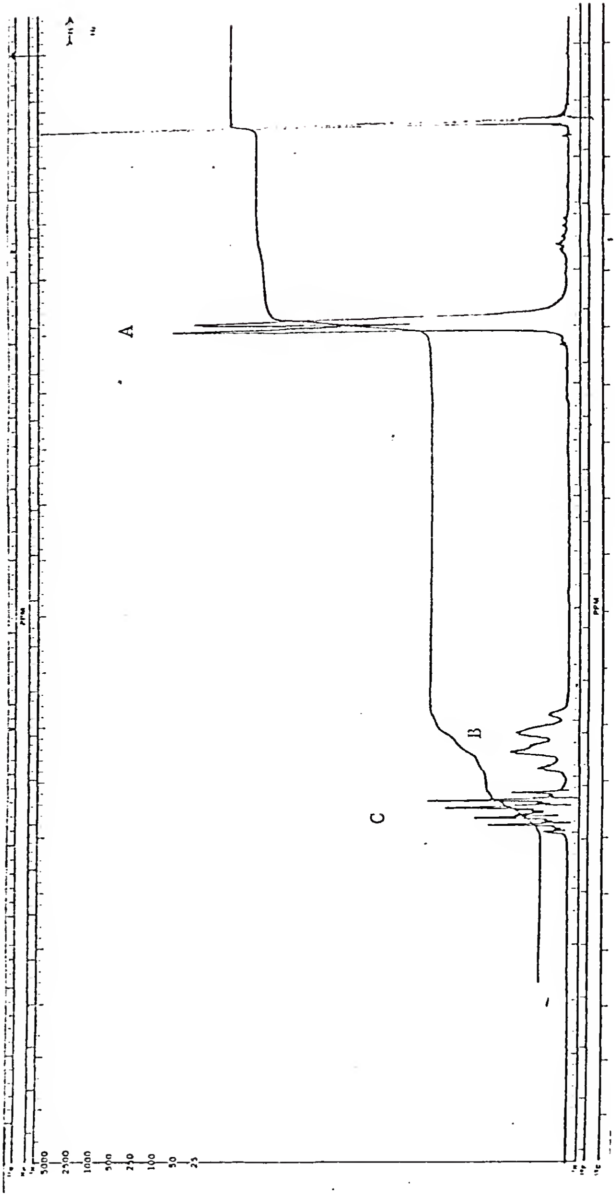


Figure 32 - H^1 NMR of $CF_2CFCH{=}CHCH_3$
$CF_2CFCH{=}CHCH_3$
C B A

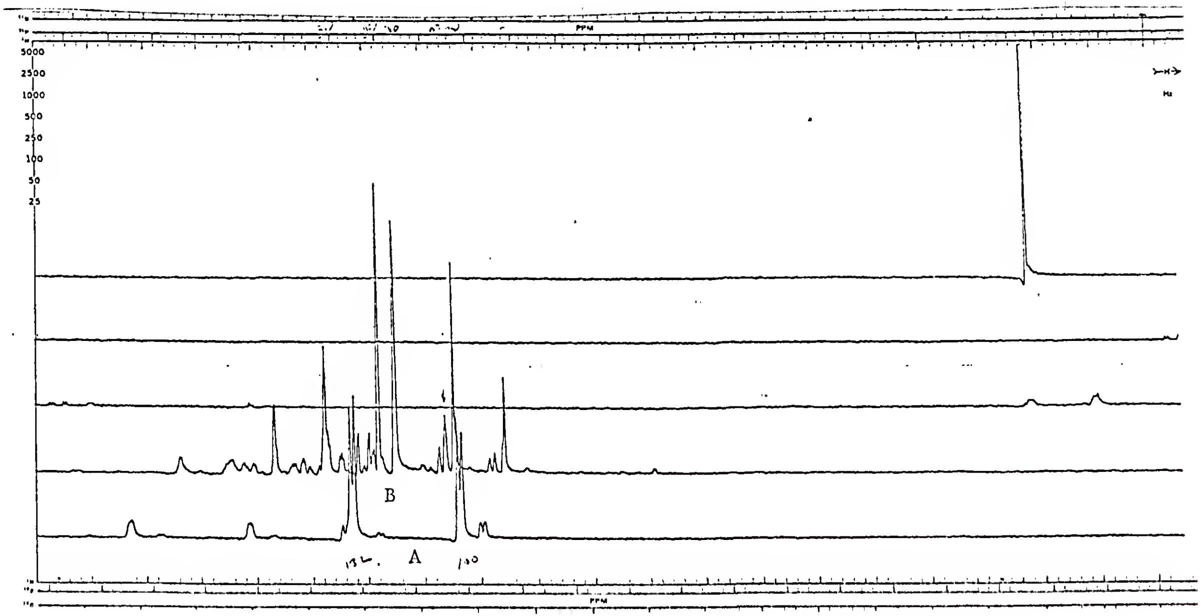
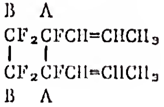


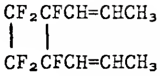
Figure 33 - F^{19} NMR of



$$\begin{array}{l} \quad\ \ B\quad\ A \\ CF_2CFCH{=}CHCH_3 \\ \ \ |\qquad\ | \\ CF_2CFCH{=}CHCH_3 \\ \quad\ \ B\quad\ A \end{array}$$

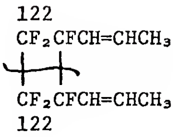
TABLE XVII

MASS SPECTRUM OF



$$\begin{array}{l}CF_2CFCH{=}CHCH_3\\ \;\;|\quad\;|\\ CF_2CFCH{=}CHCH_3\end{array}$$

Molecular Weight 244. Listing of peak with >1% base peak intensity along with $M^{\oplus}$ peak.



Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
244	0.1 $M^{\oplus}$	73	2.3
197	2.0	72	12.9
135	2.3	71	8.0
133	1.6	70	1.5
129	3.2	69	5.1
127	2.2	65	1.8
123	5.9	59	1.0
122	100.0	58	1.2
121	10.4	57	3.7
115	1.0	55	1.2
109	1.9	53	13.9
107	1.2	52	1.0
103	4.3	51	6.0
102	6.1	50	1.2
101	6.5	47	1.4
95	4.5	46	1.2
91	5.4	44	4.2
89	1.4	43	1.8
83	1.7	41	3.0
81	1.4	40	6.5
77	3.3	39	5.4
76	1.0	32	93.5
75	2.8	29	3.8

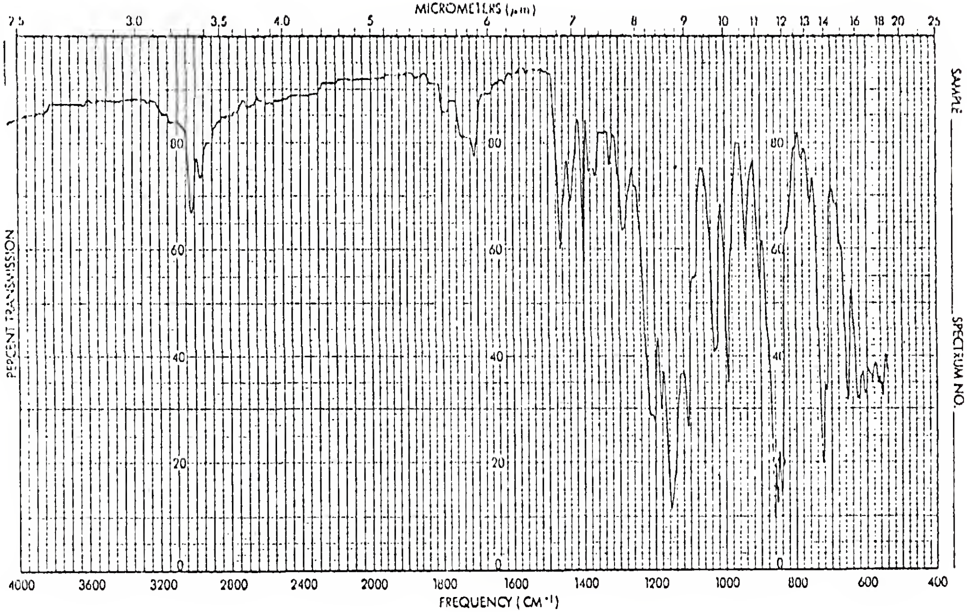
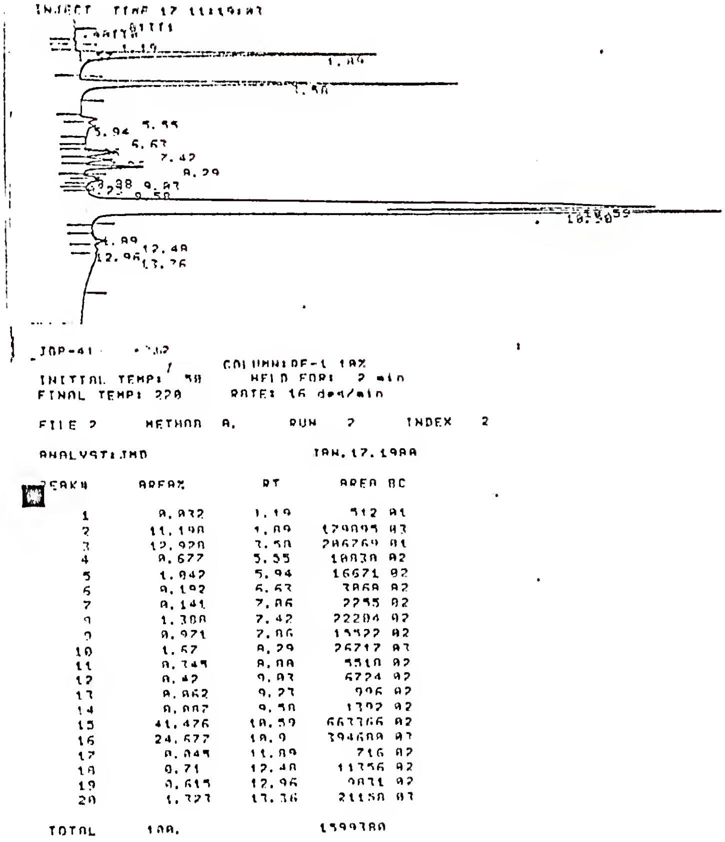


Figure 34 - Infrared Spectrum of $CCl_3CF_2CFBrCH_2CHBrCH_3$



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 FINAL TEMP: 220          RATE: 16 deg/min

 FILE 2      METHOD  0.        RUN    2        INDEX   2

 ANALYST:JMD                        JAN.17.1988

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      2        11.198        1.89       179095 03
      3        12.928        3.50       206769 01
      4         0.677        5.55        10830 02
      5         1.042        5.94        16671 02
      6         0.192        6.63         3068 02
      7         0.141        7.06         2255 02
      8         1.388        7.42        22204 02
      9         0.971        7.86        15522 02
     10         1.67         8.29        26717 03
     11         0.345        8.88         5518 02
     12         0.42         9.03         6724 02
     13         0.062        9.27          996 02
     14         0.087        9.50         1392 02
     15        41.476       10.59       663366 02
     16        24.677       10.9        394680 03
     17         0.045       11.89          716 02
     18         0.71        12.48        11356 02
     19         0.615       12.96         9831 02
     20         1.323       13.36        21158 03

  TOTAL      100.                      1599380
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Figure 35 - GLC of $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$ Two Diastereomers

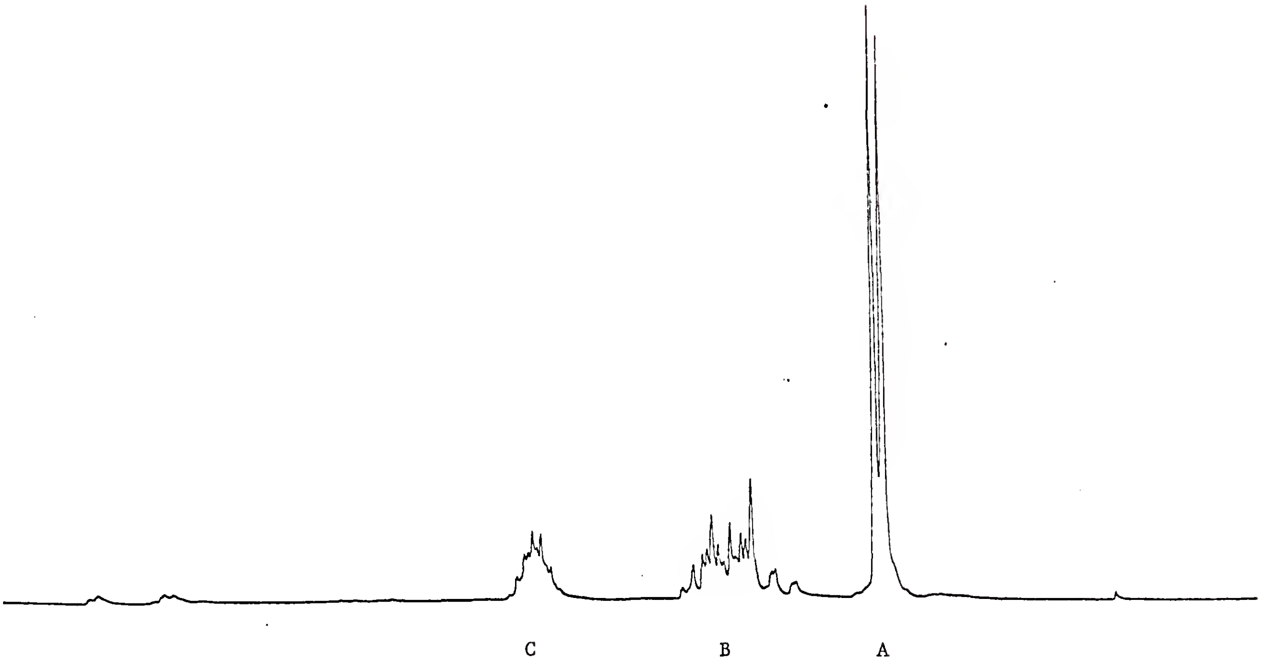


Figure 36 - H^1 NMR of $CCl_3CF_2\overset{*}{C}FBr\underset{B}{CH_2}\underset{C}{\overset{*}{C}H}Br\underset{A}{CH_3}$

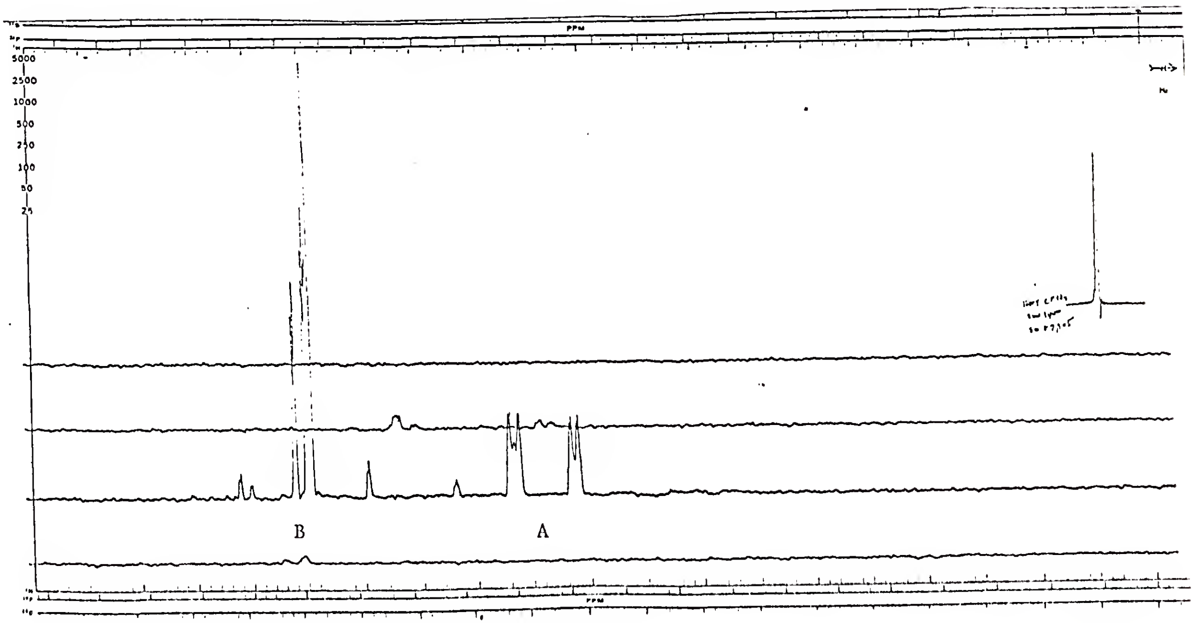
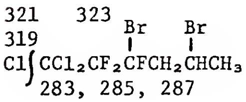


Figure 37 - F^{19} NMR of $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$
B A

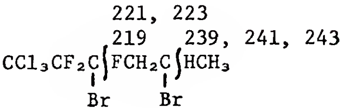
TABLE XVIII

MASS SPECTRUM OF $CCl_3CF_2\overset{*}{C}FBrCH_2\overset{*}{C}HBrCH_3$

Molecular Weight 400. Listing of all peaks >1% base intensity along with $M^{\oplus}$ peak.



$\mathrm{Cl}\big|\mathrm{CCl_2CF_2\overset{Br}{C}FCH_2\overset{Br}{C}HCH_3}$



$\mathrm{CCl_3CF_2\underset{Br}{C}\big|FCH_2\underset{Br}{C}\big|HCH_3}$

Nominal Base	% Int. Base	Nominal Base	% Int. Base
402	0.7 $M^{\oplus}$	195	1.2
400	0.5	193	1.6
398	0.2	191	1.8
323	2.7	189	3.8
321	4.1	187	3.1
319	2.1	[Peaks >5% Base Int.]	
287	1.4	177	5.4
285	3.4	167	5.3
283	2.5	153	6.8
243	1.8	151	7.1
241	5.3	145	9.6
239	6.6	143	10.1
237	1.8	132	5.1
235	1.3	129	10.9
225	1.4	127	13.4
223	4.9	125	5.1
221	7.2	123	6.8
219	3.8	122	6.1
207	1.9	121	11.6
206	1.1	119	13.2
205	4.5	117	12.7
204	1.7	111	12.6
203	7.7	109	68.5
201	3.5	107	100.0

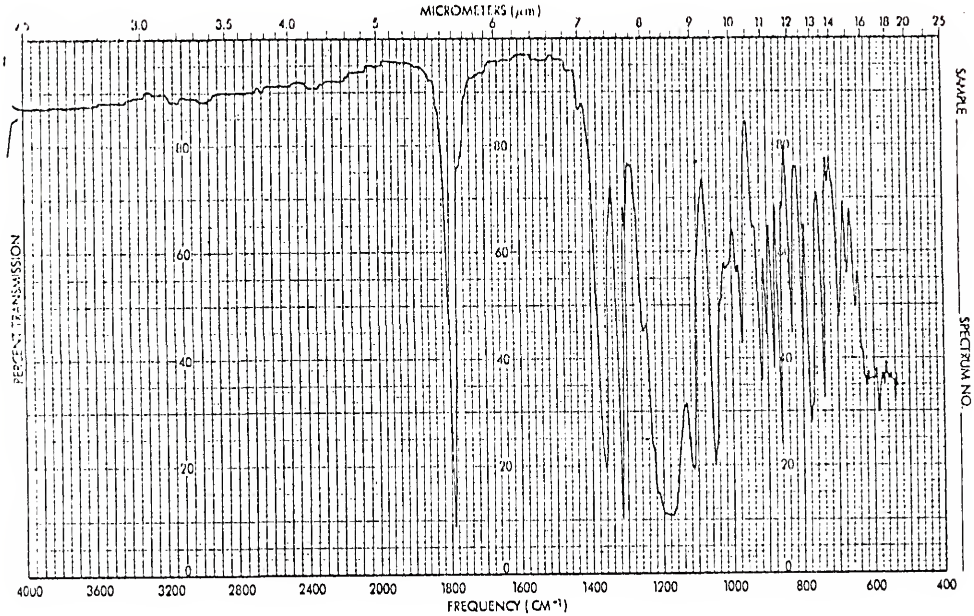


Figure 38 - Infrared of $CF_2BrCFBrCF_2CF=CF_2$

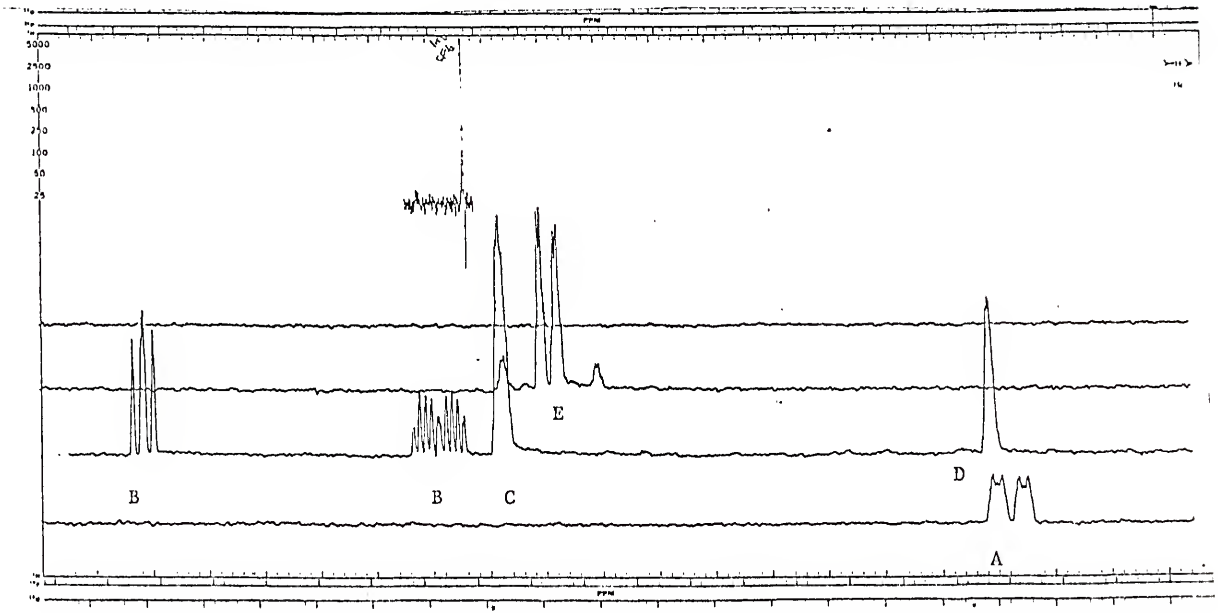


Figure 39 - F^{19} NMR of $CF_2Br\overset{*}{C}FBrCF_2CF=CF_2$
E D C A B

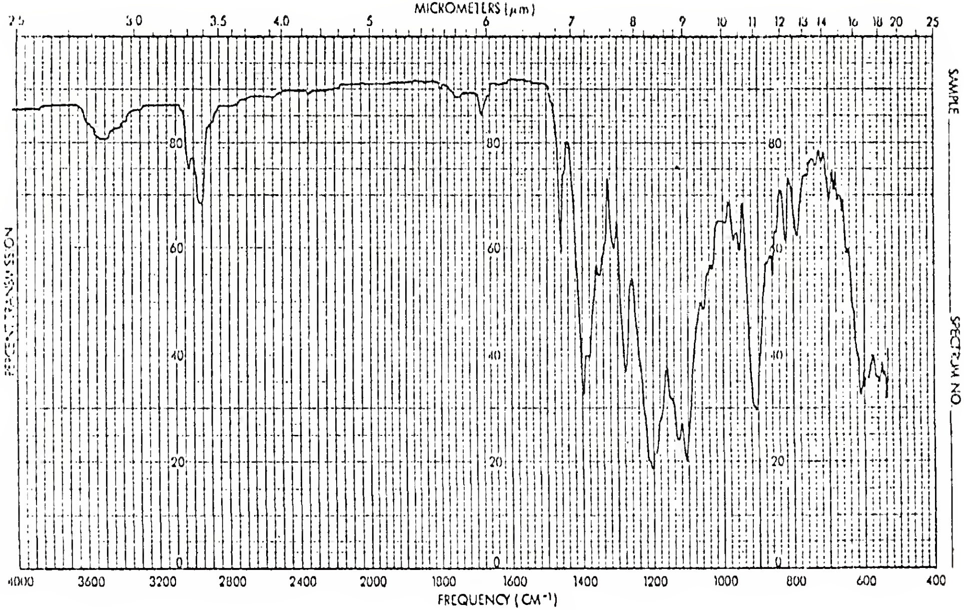
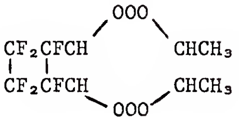


Figure 40 - Infrared Spectrum of



Ozonolysis Product

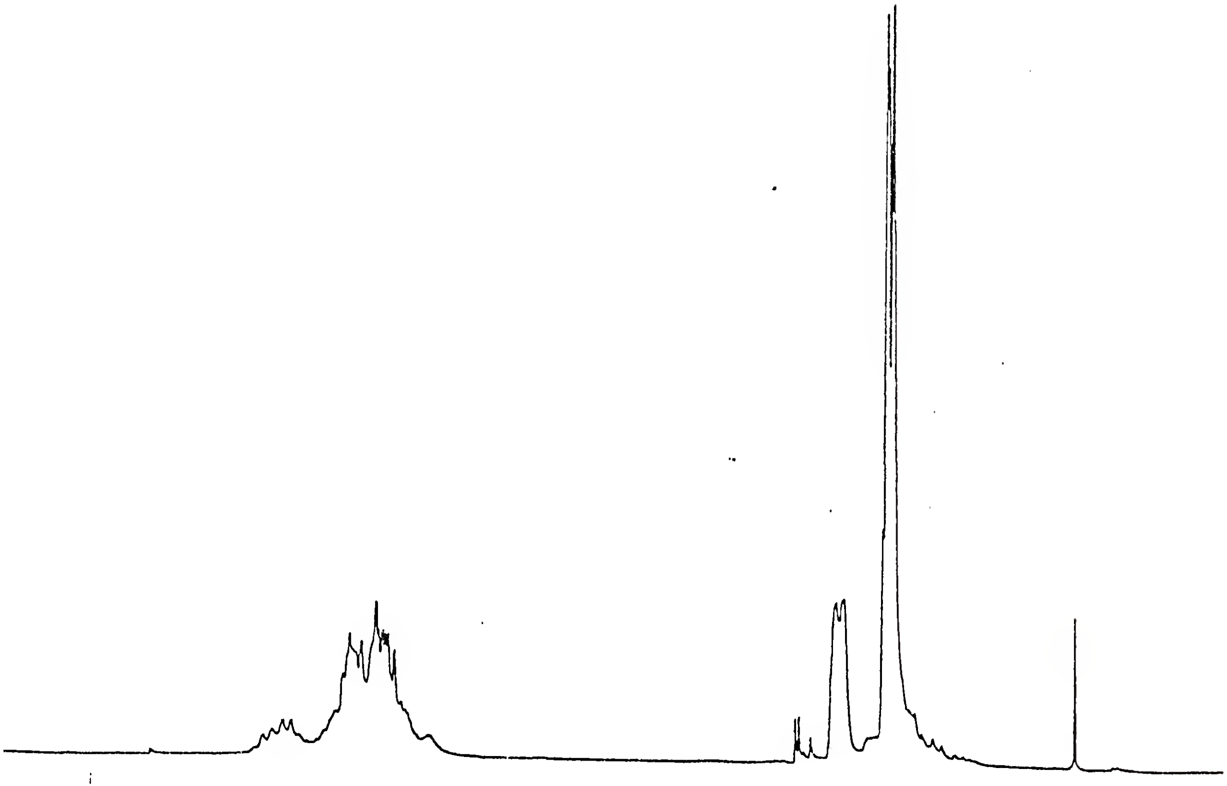


Figure 41 - H^1 NMR of $\begin{array}{l} CF_2CFCH{=}CHCH_3 \\ | \quad\;\; | \\ CF_2CFCH{=}CHCH_3 \end{array}$ Ozonide

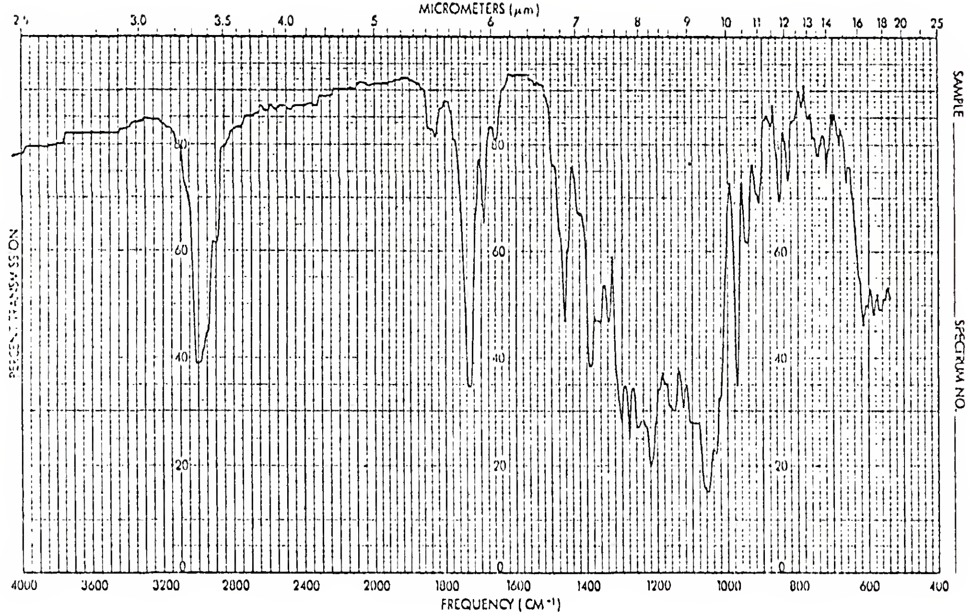


Figure 42 - Infrared Spectrum of $C_2H_5OCF_2CF{=}CHCH_2CH_3$ (85%) and $C_2H_5OCF_2CFHCH{=}CHCH_3$ (15%)

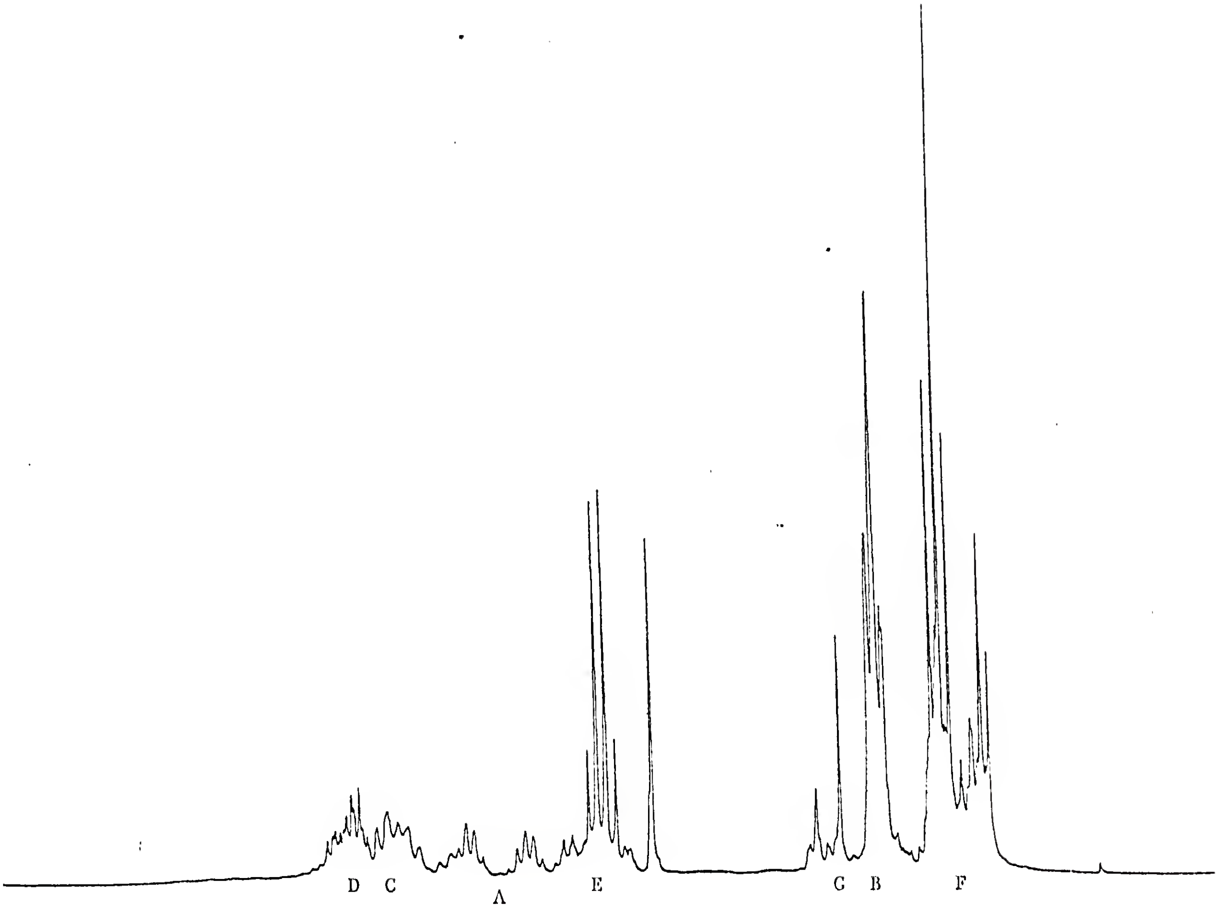


Figure 43 - H^1 NMR of $\underset{F}{CH_3}\underset{E}{CH_2}OCF_2\underset{A}{CFH}\underset{D}{CH}=\underset{C}{CH}\underset{B}{CH_3}$ and $\underset{F}{CH_3}\underset{E}{CH_2}OCF_2CF=\underset{G}{CH}\underset{F}{CH_2}CH_3$

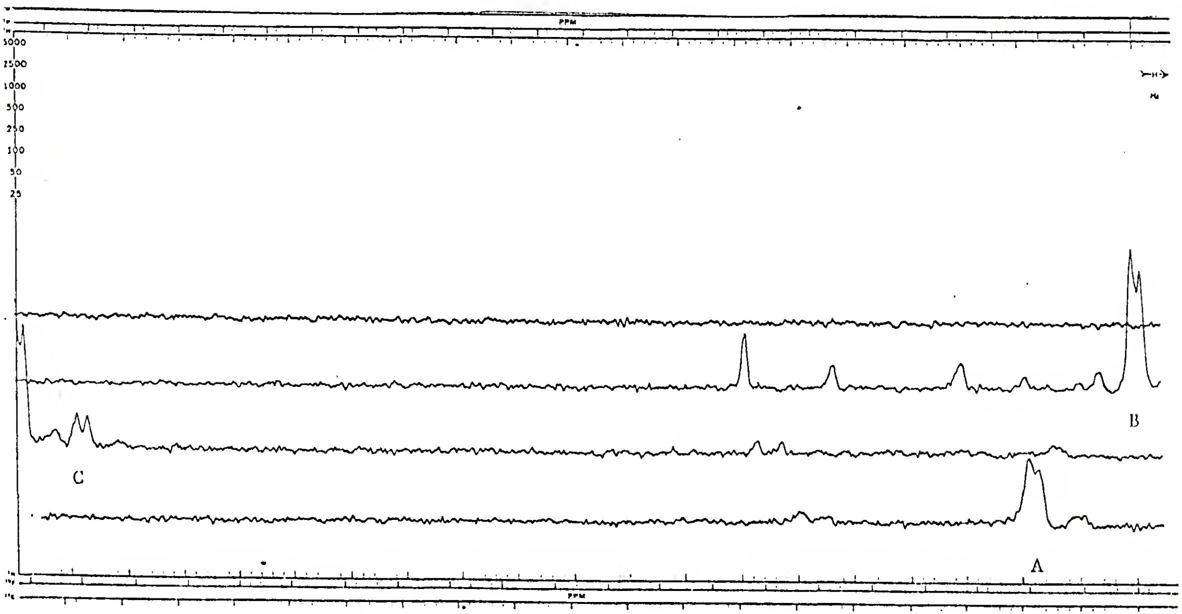
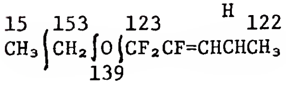


Figure 44 - F^{19} NMR of $CH_3CH_2OCF_2CFHCH{=}CHCH_3$ and $CH_3CH_2OCF_2CF{=}CHCH_2CH$
B A B C

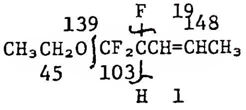
TABLE XIX

MASS SPECTRUM OF $CH_3CH_2OCF_2CFHCH=CH_3$ and $CH_3CH_2OCF_2CF=CHCH_2CH_3$ MIXTURE

Molecular Weight 168. Listing of peaks with >0.5% base peak intensity along with $M^{\oplus}$ peak.



$CH_3CH_2OCF_2CF=CHCHCH_3$



$CH_3CH_2OCF_2CCH=CHCH_3$

Nominal Mass	% Int. Base
168	0.5 $M^{\oplus}$
155	0.8
153	4.8
151	5.6
149	0.5
148	2.9
146	0.9
139	0.5
135	1.6
134	2.7
132	0.6
129	0.6
123	1.1
122	4.8
121	2.2
120	8.8
119	2.2
118	3.0
117	1.2
116	0.8
115	0.6
111	0.6
108	0.5

Nominal Mass	% Int. Base
107	0.9
106	0.5
105	2.0
104	2.1
103	12.3
102	2.2
101	13.1
100	4.7
99	3.1
95	20.6
Peak intensity >1%	
93	1.5
91	3.2
90	2.4
89	2.3
87	5.5
85	7.2
83	3.3
82	2.5
81	28.1
80	1.3
77	6.7

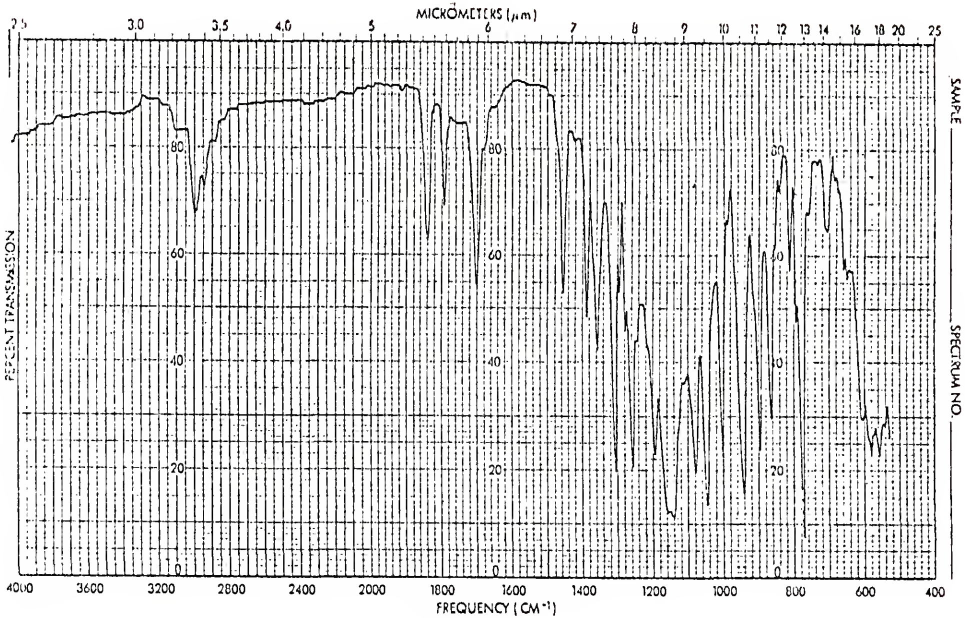


Figure 45 - Infrared Spectrum of $CF_2BrCFBrCH=CHCH_3$

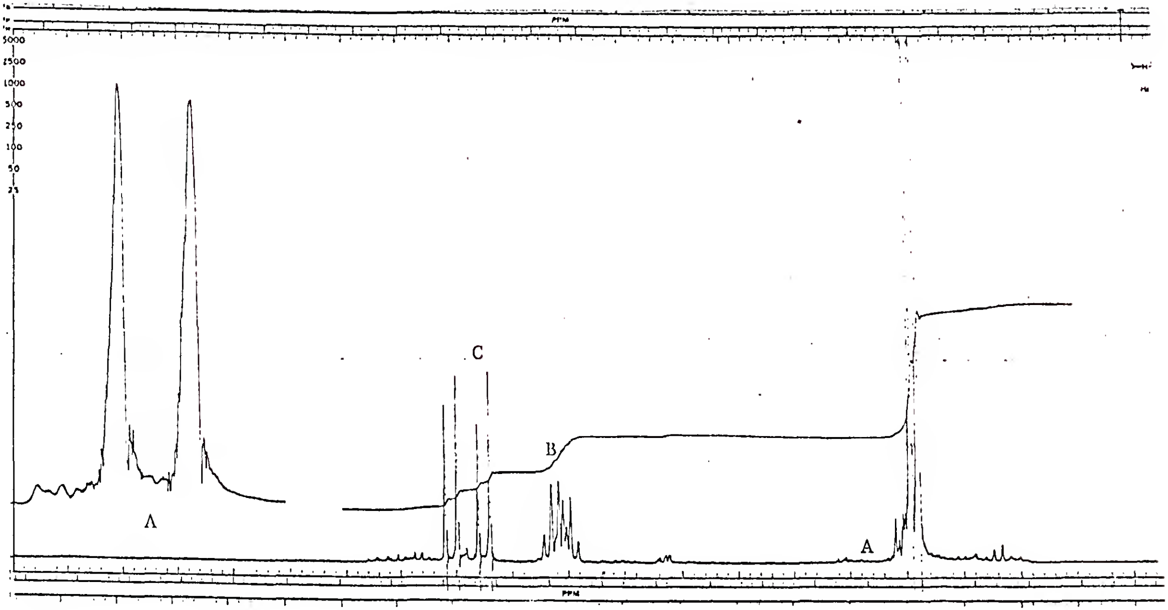
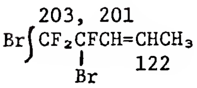


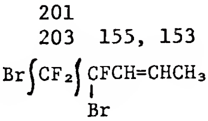
Figure 46 - H^1 NMR of $CF_2Br\overset{*}{C}FBrCH{=}CHCH_3$
C B A

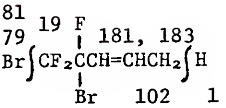
TABLE XV

MASS SPECTRUM OF $CF_2BrCFBrCH=CHCH_3$

Molecular Weight 282. Listing of all peaks with >1% base intensity along with $M^{\oplus}$ peak.







Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
283	0.2 $M^{\oplus}$	151	3.2
282	0.1	139	5.1
281	0.5	138	1.9
219	2.3	137	5.9
217	1.9	131	3.8
204	5.4	129	3.3
203	98.4	123	7.1
202	5.5	122	77.0
201	100.0	121	30.5
188	1.8	120	1.9
186	1.8	119	5.5
184	2.6	113	1.3
183	6.4	111	1.5
182	2.7	109	1.1
181	6.0	107	3.9
175	1.4	106	1.6
173	1.5	103	7.5
157	3.8	102	14.9
155	3.9	101	28.3
153	3.2	95	25.2

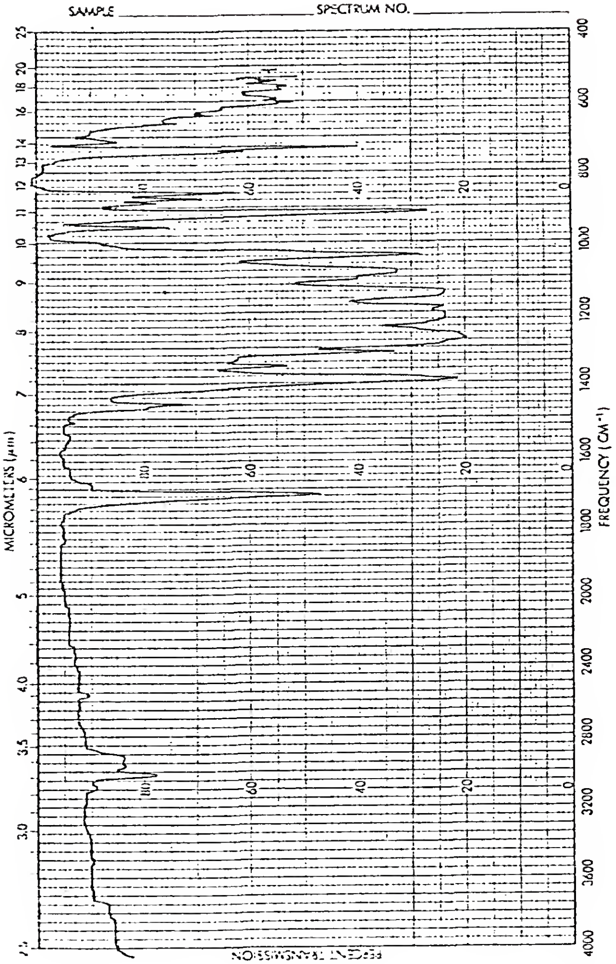
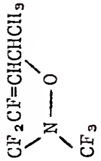


Figure 47 - Infrared of



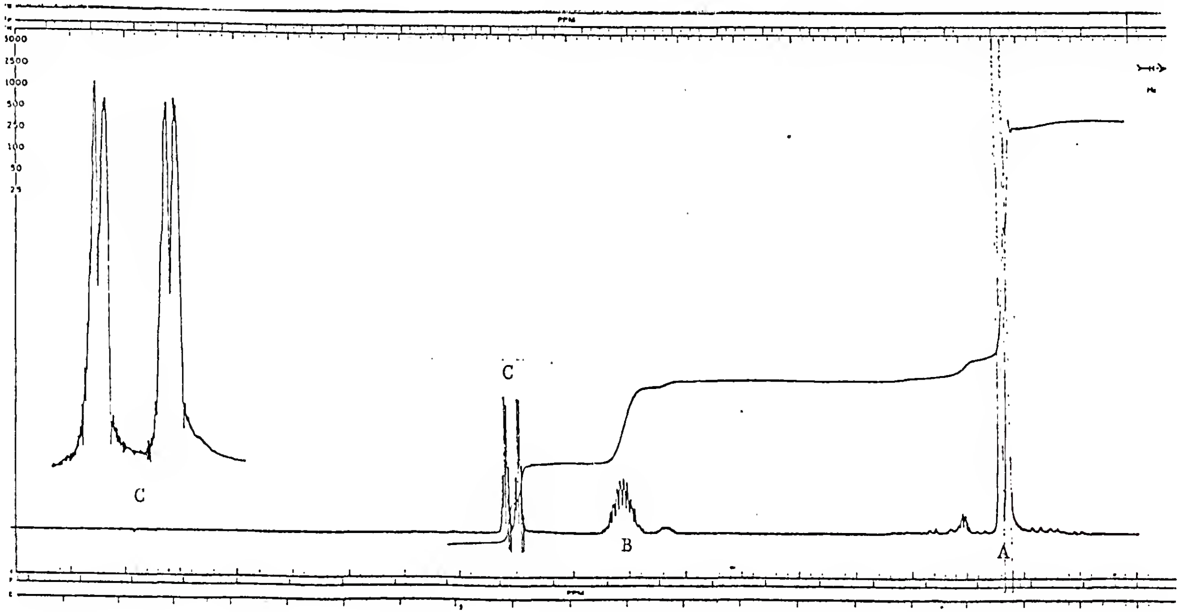
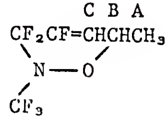


Figure 48 - H^1 NMR of



$$\overset{C}{C}F_2CF{=}\overset{B}{C}H\overset{A}{C}HCH_3 \quad (\text{ring: } CF_2 - N(CF_3) - O - CH)$$

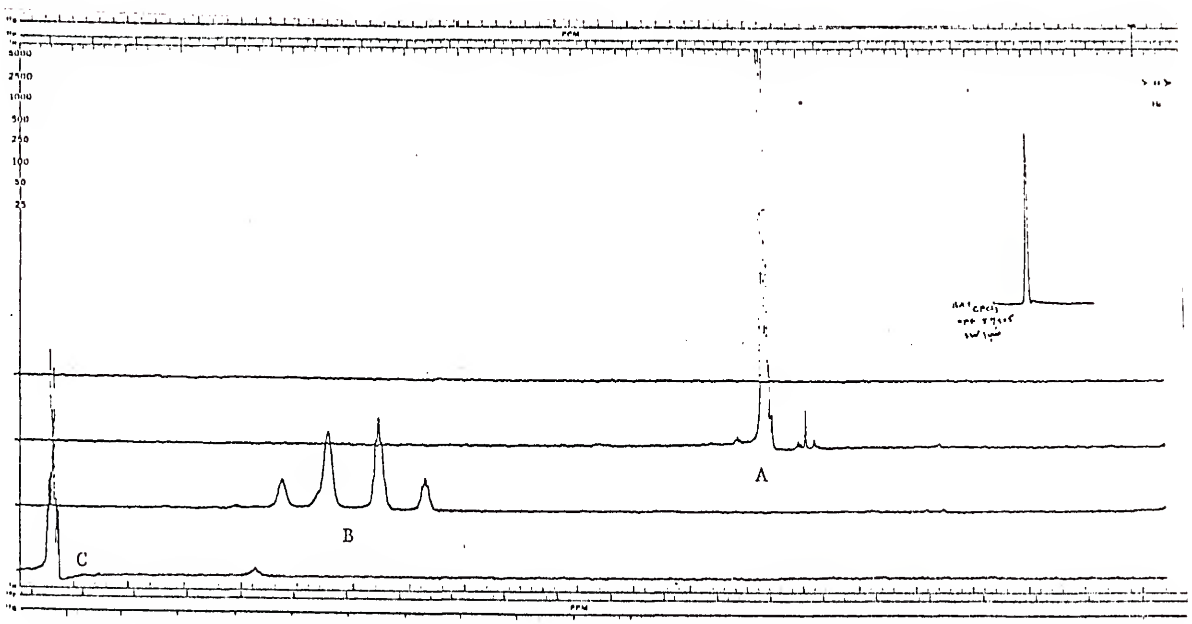


Figure 49 - F^{19} NMR of

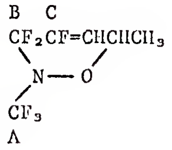
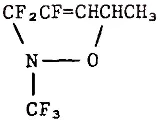
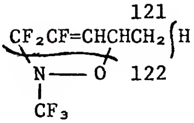


TABLE XXI

MASS SPECTRUM OF



Molecular Weight 221. Listing for peaks >1% base peak intensity along with $M^{\oplus}$ peak.



Nominal Mass	% Int. Base
221	2.5 $M^{\oplus}$
182	2.8
156	2.4
123	5.8
122	100.0
121	10.9
118	1.3
114	1.9
109	1.0
103	2.4
102	5.2
101	6.8
96	1.6
95	5.0
94	1.5
91	2.9
89	2.5
77	2.4
76	1.7
75	3.3
73	1.5
72	19.4
71	10.8
70	1.8
69	34.3

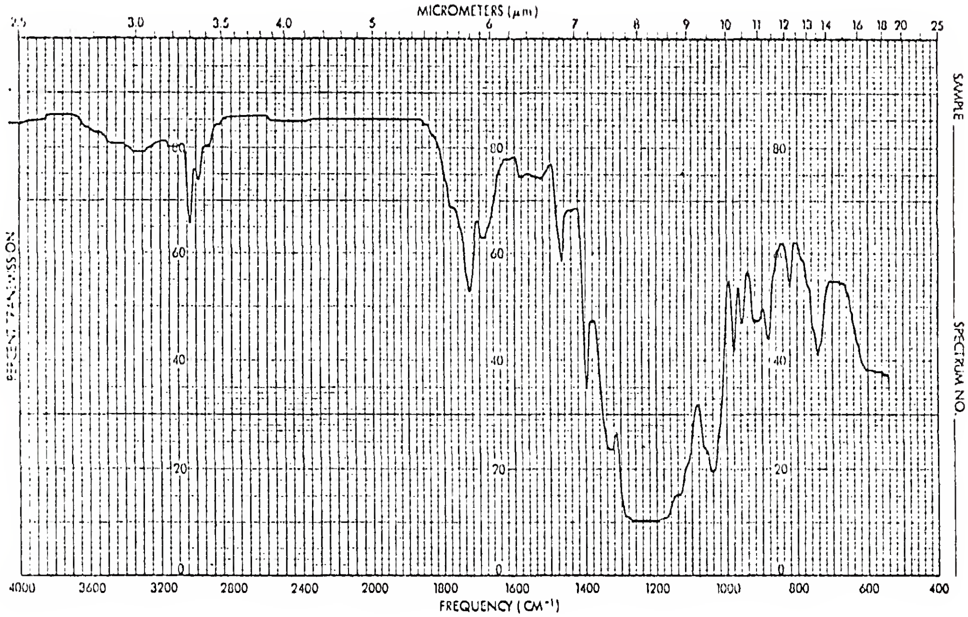


Figure 50 - Infrared Spectrum of Polymer from Reaction of CF_3NO and CF_2=CFCH=$CHCH_3$

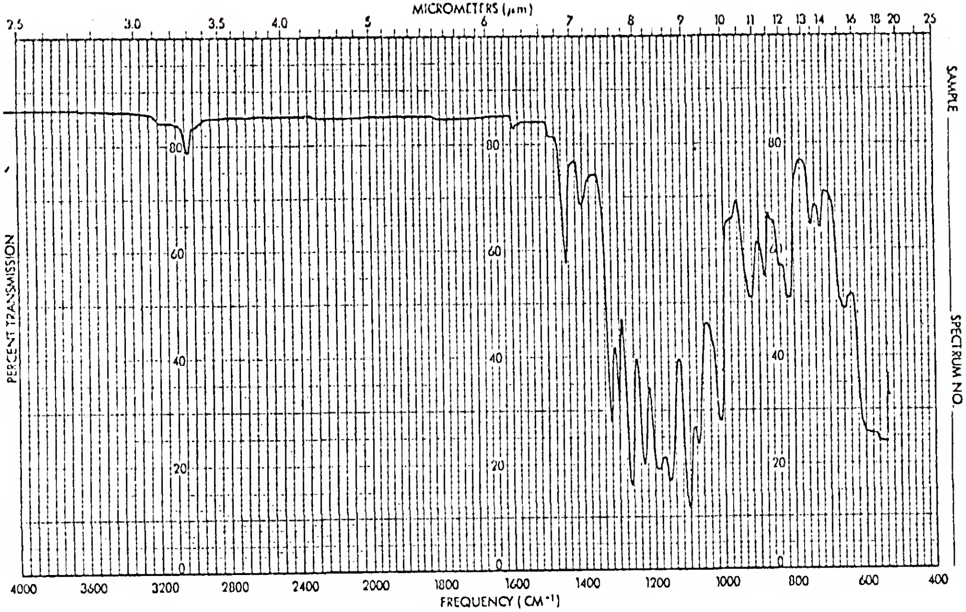


Figure 51 - Infrared Spectrum of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$

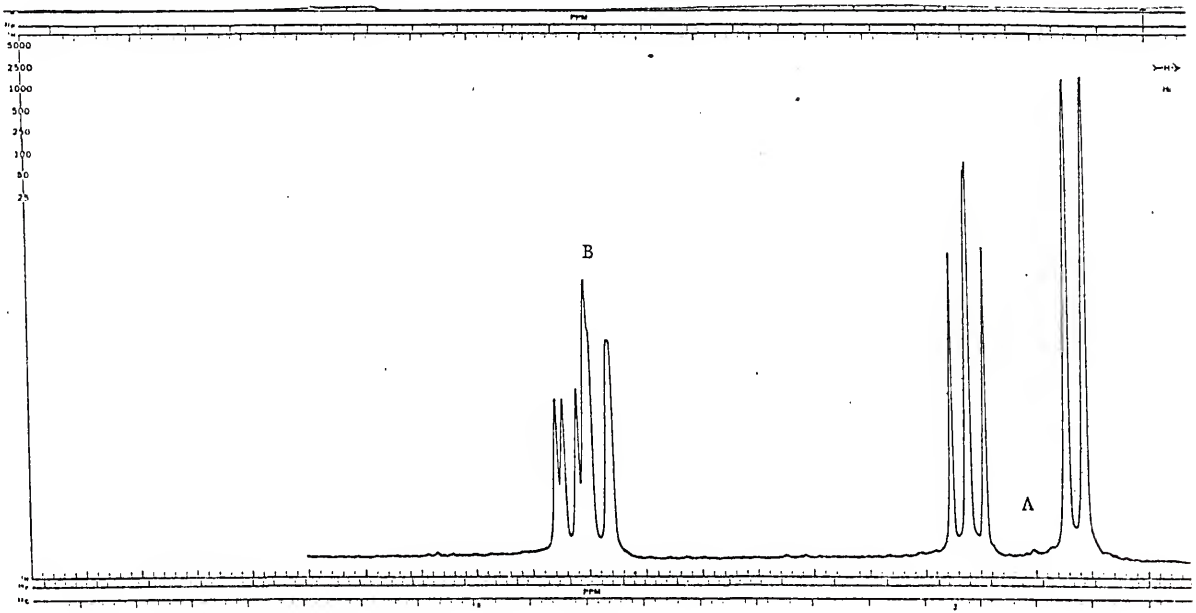


Figure 52 - F^{19} NMR of $\underset{B}{CF_2Cl}\overset{*}{C}FClCH_2\overset{*}{C}HI\underset{A}{CF_3}$

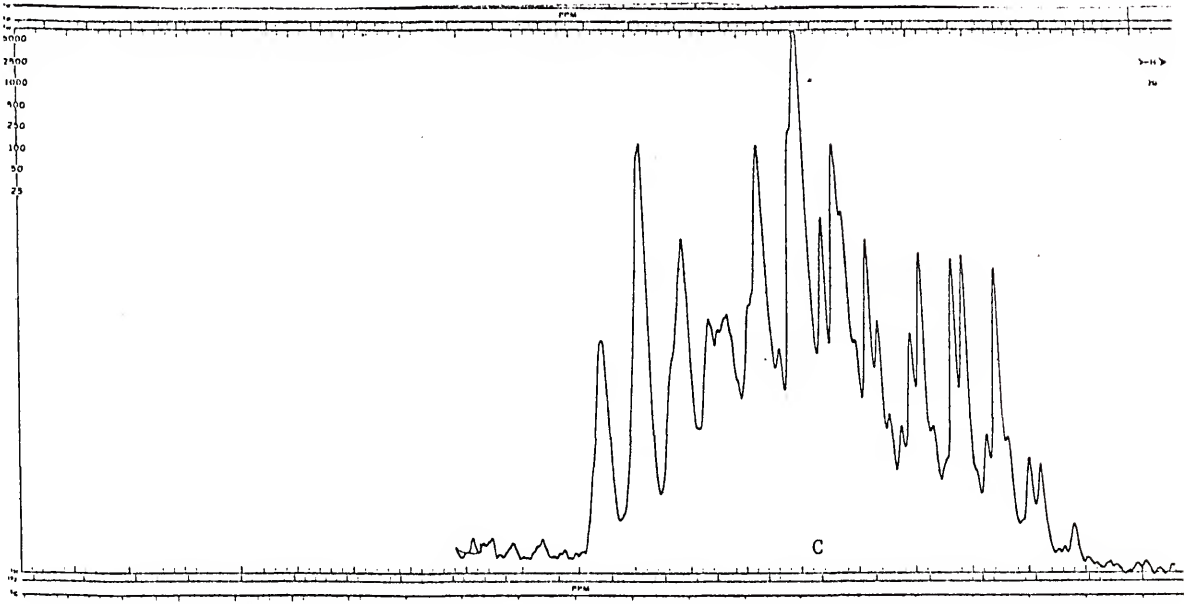


Figure 53 - F^{19} NMR of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$
C

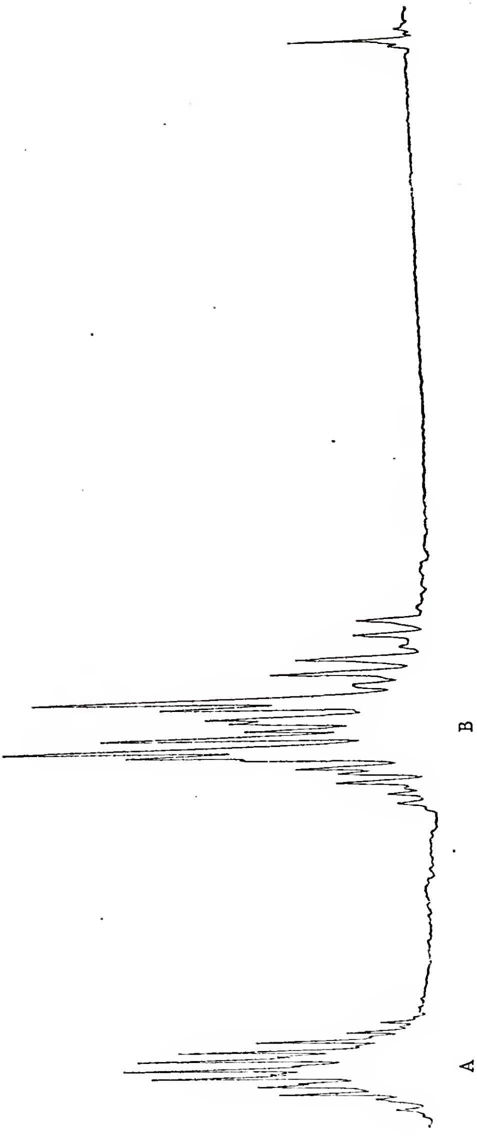
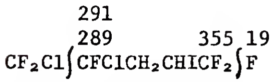


Figure 54 - H^1 NMR of $CF_2Cl\overset{*}{C}FClCH_2\overset{*}{C}HICF_3$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ B $\quad$ A

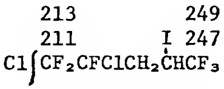
TABLE XXII

MASS SPECTRUM OF $CF_2ClCFClCH_2CHICF_3$

Molecular Weight 376. Isotopes of Cl and I give parent peaks with M/E 374, 375, 376, 378. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$CF_2Cl\overset{\substack{291\\289}}{\Big\vert}CFClCH_2CHICF_2\overset{355\ 19}{\Big\vert}F$$



$$Cl\overset{\substack{213\\211}}{\Big\vert}CF_2CFClCH_2\overset{\substack{249\\I\ 247}}{C}HCF_3$$

Nominal Mass	% Int. Base	
378	9.6	
376	66.0	$M^{\oplus}$
375	5.0	
374	91.7	
355	0.7	
291	5.5	
290	0.7	
289	16.3	
281	0.8	
280	1.1	
278	1.6	
259	1.4	
257	2.7	
254	0.9	
253	2.9	
251	3.9	
250	1.3	
249	21.1	
248	1.9	
247	33.1	
245	1.0	
243	3.1	
241	3.3	
231	1.7	
230	1.9	
229	9.8	
228	2.8	
227	15.9	
225	1.2	
224	1.1	
223	24.1	
222	2.1	
221	1.3	
219	0.9	
214	2.5	
213	31.6	
212	7.9	
211	100.0	
210	1.4	
209	23.9	
208	1.7	
207	7.5	
205	2.1	
204	28.3	
203	7.3	
[>5% Base Intensity]		
193	11.6	
192	7.8	
191	10.3	
177	57.6	
176	6.9	
175	6.1	
164	7.6	
163	14.5	
162	20.6	
161	36.2	
159	8.8	
157	6.9	
153	14.7	
151	30.6	
149	29.1	
147	9.3	
145	7.9	
143	6.1	
142	5.0	
135	6.6	
133	49.7	
131	13.6	
129	9.4	
128	25.0	
127	59.6	
126	10.9	
119	5.2	
117	14.8	
116	12.5	
113	49.5	
111	22.7	
103	9.7	
101	15.0	
96	5.7	
95	31.6	

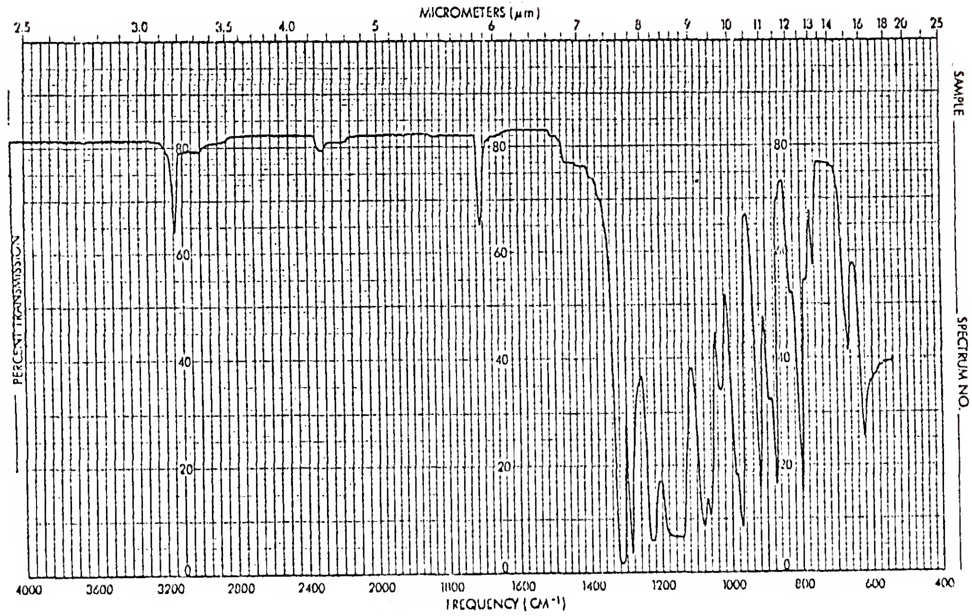


Figure 55 - Infrared Spectrum of $CF_2ClCFClCH=CHCF_3$

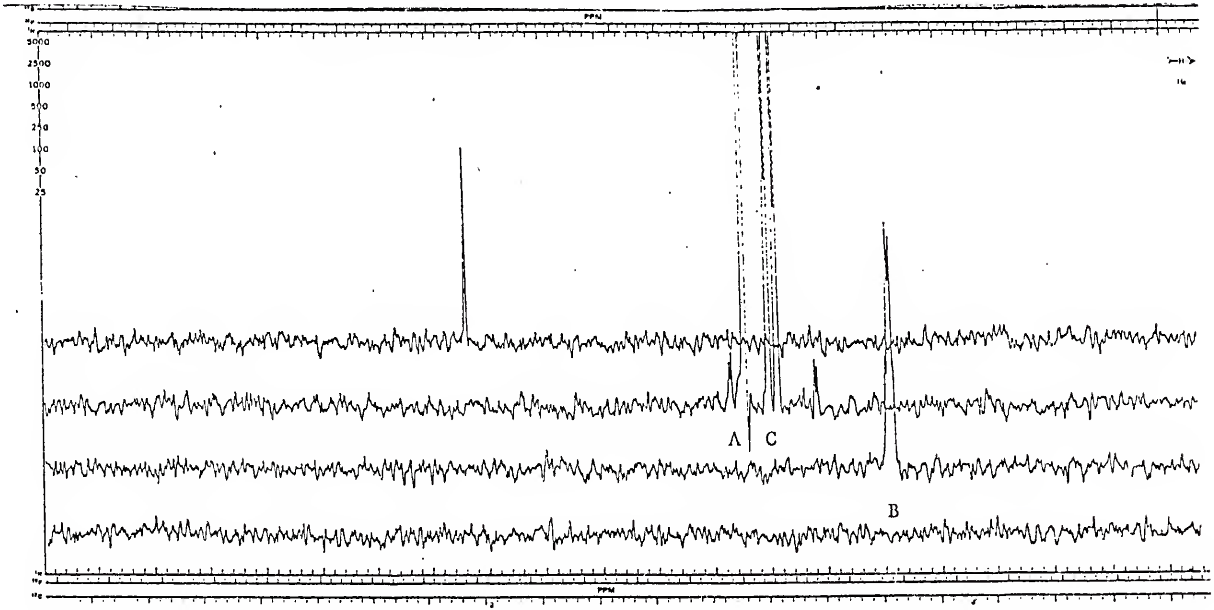
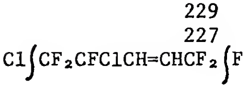


Figure 56 - F^{19} NMR of $\underset{C}{CF_2Cl}\underset{B}{\overset{*}{C}FCl}CH{=}CH\underset{A}{CF_3}$

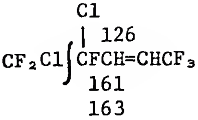
TABLE XXIII

MASS SPECTRUM OF $CF_2ClCFClCH{=}CHCF_3$

Molecular Weight 246. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$\mathrm{Cl}\int\mathrm{CF_2CFClCH{=}CHCF_2}\overset{\substack{229\\227}}{\int}\mathrm{F}$



$\mathrm{CF_2Cl}\int\overset{\substack{\mathrm{Cl}\\|\ 126}}{\underset{\substack{161\\163}}{\mathrm{C}}}\mathrm{FCH{=}CHCF_3}$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
246	0.1 $M^{\oplus}$	142	3.0
229	1.4	141	1.0
227	2.3	137	1.5
213	7.4	131	1.1
212	1.3	129	3.1
211	23.6	127	1.0
209	1.0	126	11.3
207	1.5	125	1.4
193	1.4	116	1.2
192	0.6	114	0.9
191	4.3	113	22.1
179	0.9	112	1.0
177	1.5	111	27.1
176	2.2	107	1.8
175	2.0	106	1.6
171	0.6	105	0.6
164	1.4	103	1.4
163	32.6	101	2.0
162	4.6	[>5% Base Int.]	
161	100.0	95	5.8
157	2.9	87	7.1
149	0.9	85	19.6
147	2.7	75	6.0
145	2.8	70	10.4
144	1.0	57	8.5
143	0.5		

Figure 57 - Infrared Spectrum of $CF_2=CFCH=CHCF_3$

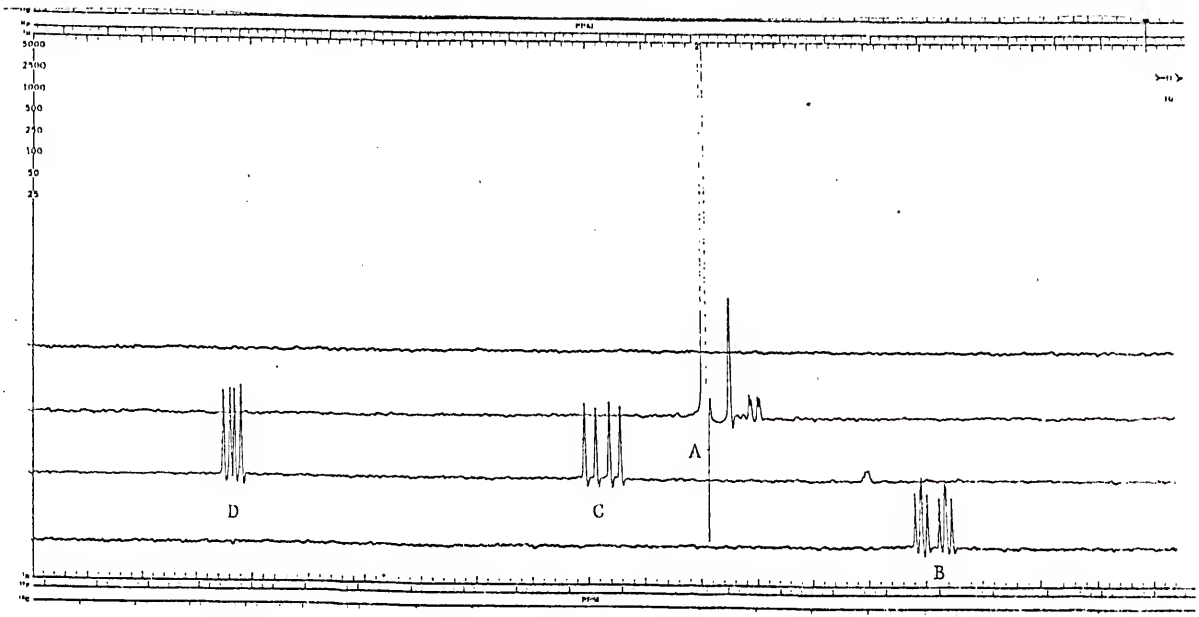
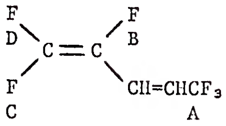


Figure 58 - F^{19} NMR of



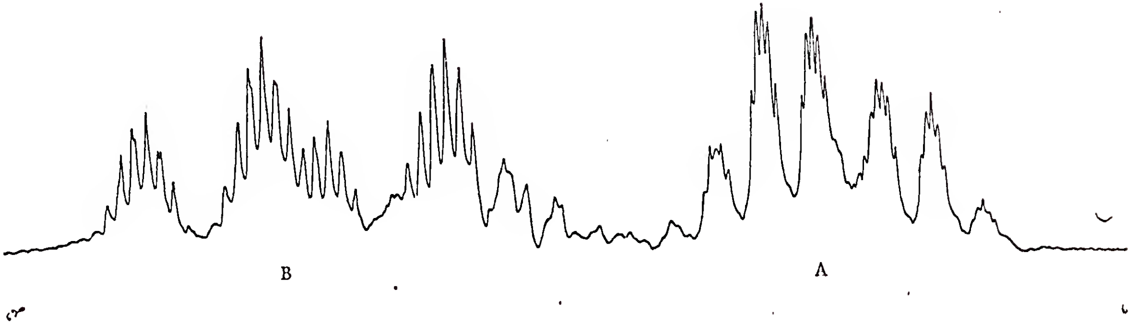
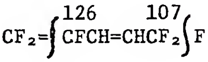


Figure 59 - H^1 NMR of $CF_2=CFC\underset{B}{H}=C\underset{A}{H}CF_3$

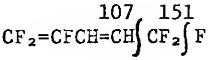
TABLE XXIV

MASS SPECTRUM OF $CF_2=CFCH=CHCF_3$

Molecular Weight 176. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$CF_2=\overset{126}{\int}CFCH=CHCF_2\overset{107}{\int}F$



$CF_2=CFCH=CH\overset{107}{\int}CF_2\overset{151}{\int}F$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
176	82.7 $M^{\oplus}$	76	3.2
163	2.4	75	21.3
161	1.0	69	35.5
158	2.0	68	1.7
157	30.3	58	1.4
145	1.9	57	48.8
138	1.3	56	13.3
137	22.5	55	2.2
127	4.3	51	5.9
126	100.0	50	1.8
125	2.7	44	2.4
123	2.2	43	7.4
113	2.9	42	3.5
107	13.1	41	7.1
106	10.1	40	1.8
105	1.0	39	1.8
100	1.5	38	4.4
95	3.6	37	3.3
93	3.2	32	24.9
88	6.8	31	10.6
87	2.9	29	3.9
83	1.7	27	2.0

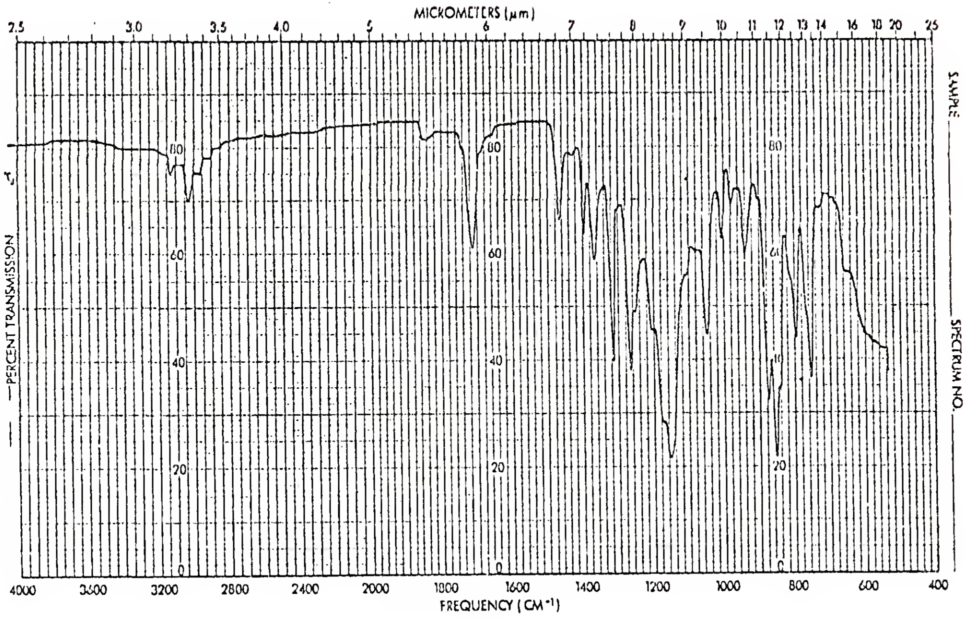


Figure 60 - Infrared Spectrum of $CCl_3CF_2CFBrCH=CHCH_3$

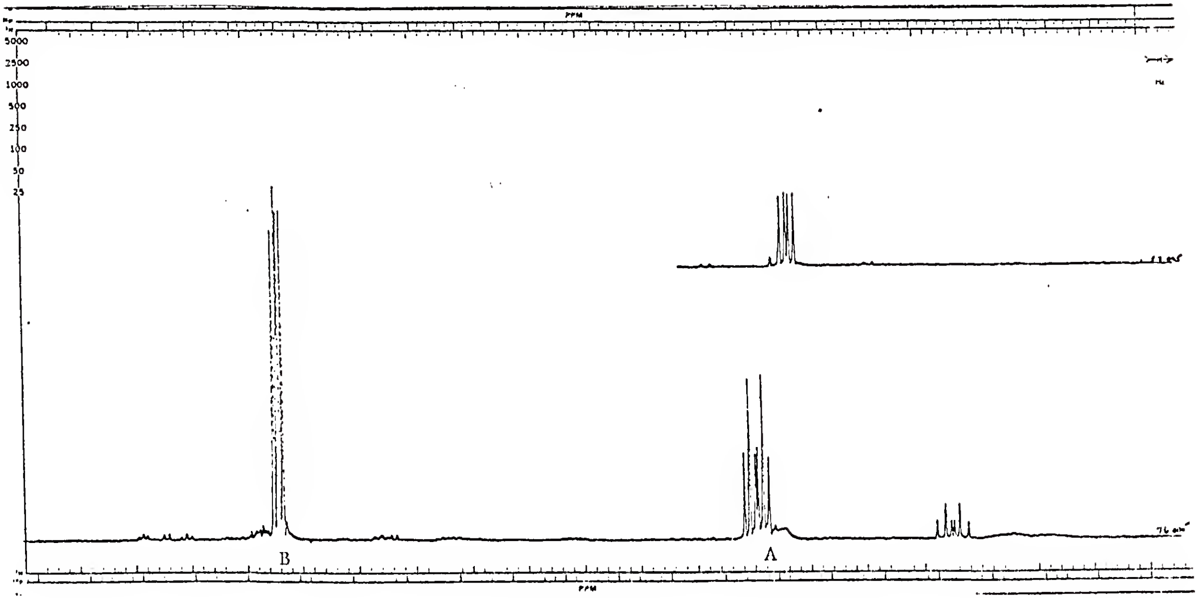


Figure 61 - F^{19} NMR of $CCl_3CF_2\overset{*}{C}FBrCH=CHCH_3$
B A

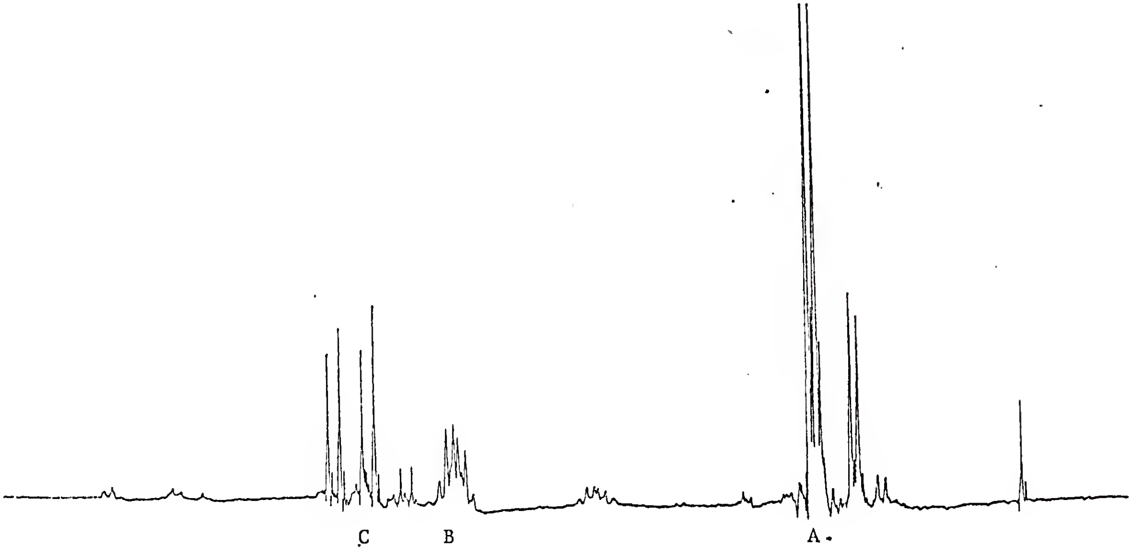
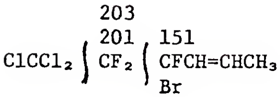


Figure 62 - H^1 NMR of $CCl_3CF_2\overset{*}{C}FBrCH{=}CHCH_3$
C B A

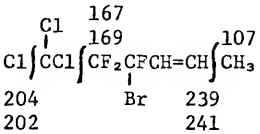
TABLE XXV

MASS SPECTRUM OF $CCl_3CF_2CFBrCH=CHCH_3$

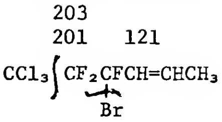
Molecular Weight 319. Listing of peaks with >0.5% base peak intensity.



$ClCCl_2 \overset{203,\,201}{\Big|} CF_2 \overset{151}{\Big|} \underset{Br}{CF}CH=CHCH_3$



$Cl \underset{204,\,202}{\Big|} \overset{Cl}{C}Cl \overset{167,\,169}{\Big|} CF_2\underset{Br}{C}FCH=CH \overset{107}{\underset{239,\,241}{\Big|}} CH_3$



$CCl_3 \overset{203,\,201}{\Big|} CF_2\overset{121}{\underset{Br}{C}}FCH=CHCH_3$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
319	No parent peak	172	0.5
285	0.7	171	2.9
283	0.5	170	1.2
245	0.7	169	6.4
244	0.5	168	2.2
243	6.1	167	2.7
242	1.3	166	1.7
241	16.8	165	1.3
240	1.3	164	1.3
239	17.1	163	1.9
225	0.6	161	0.8
223	0.8	159	0.9
221	0.5	158	1.3
219	0.6	157	2.0
209	0.9	156	1.4
207	1.4	[>5% Int. Base]	
206	1.9	133	6.7
205	2.8	131	8.2
204	3.6	129	22.2
203	16.7	122	22.8
202	1.0	121	23.7
201	15.0	119	23.7
199	1.7	117	22.9
193	0.5	109	33.7
191	1.9	108	5.1
189	2.3	107	100.0
187	1.0	102	6.4
185	1.1	101	13.3
184	0.5	95	9.0
183	2.6	91	5.0
181	2.1	83	5.3
179	0.6	77	5.2
177	0.6	75	5.6
175	0.8	72	6.2
173	1.7	71	11.6
		69	8.3

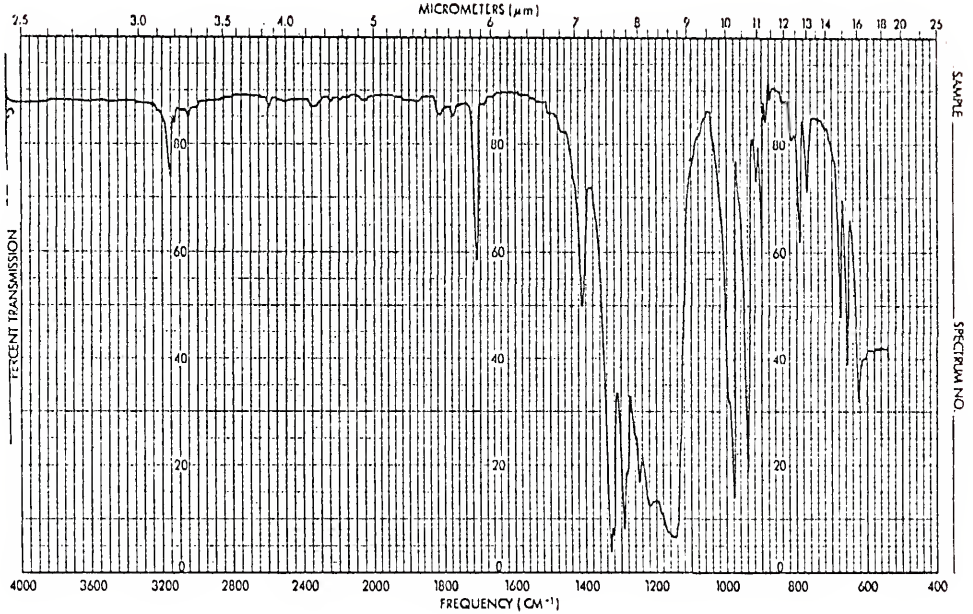
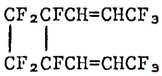


Figure 63 - Infrared Spectrum of



$$\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ \;\,|\quad\;| \\ CF_2CFCH{=}CHCF_3 \end{array}$$

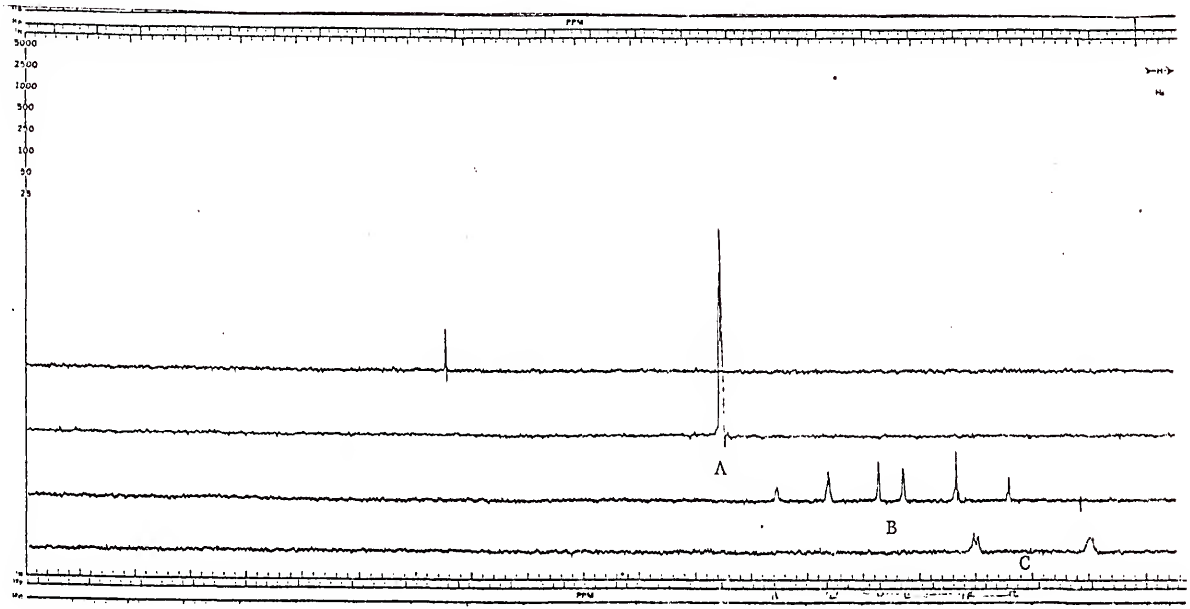
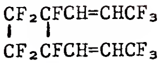


Figure 64 - F^{19} NMR of

$$\begin{array}{l} \text{B}\ \ \ \text{C}\qquad\ \ \ \text{A} \\ CF_2CFCH{=}CHCF_3 \\ \ |\quad\ | \\ CF_2CFCH{=}CHCF_3 \\ \text{B}\ \ \ \text{C}\qquad\ \ \ \text{A} \end{array}$$

TABLE XXVI

MASS SPECTRUM OF



$$\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ \,|\quad\;\; | \\ CF_2CFCH{=}CHCF_3 \end{array}$$

Molecular Weight 352. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.

Nominal Mass	% Int. Base
352	0.1 $M^{\oplus}$
252	1.1
213	1.5
207	2.3
183	5.0
177	5.2
176	100.0
163	8.4
161	3.2
158	1.3
157	24.5
145	8.1
137	2.9
133	1.2
127	2.7
126	61.6
125	1.2
119	2.1
114	1.5
113	3.4
111	1.1
107	3.2
106	1.9
100	1.2
95	5.8
93	1.0
88	2.0
85	1.0
75	6.0
69	16.2
57	8.2
56	1.1
51	4.5
44	1.0
40	1.3
32	22.0
31	2.5

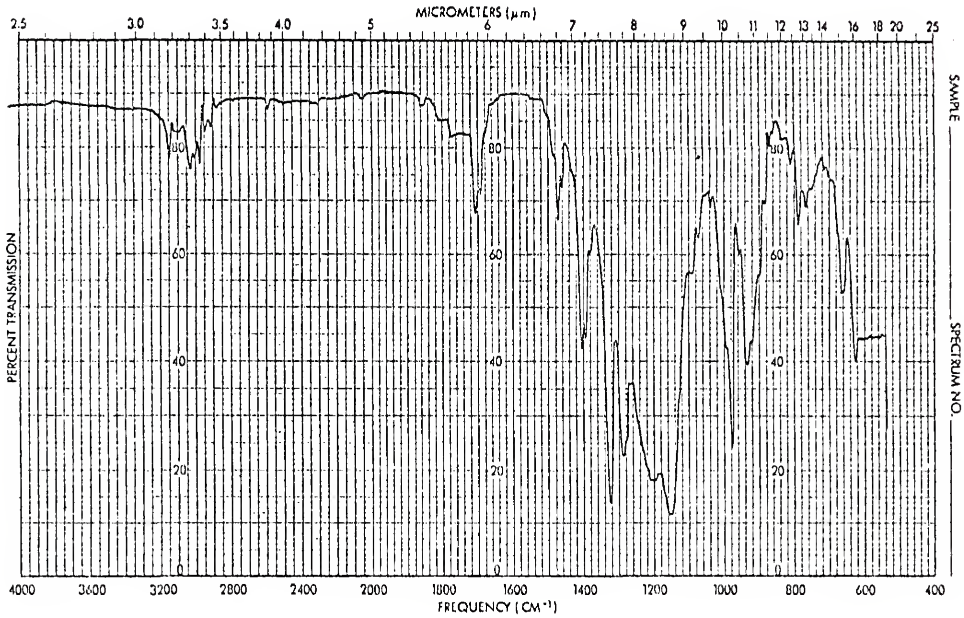


Figure 65 - Infrared Spectrum of $\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ | \quad\;\; | \\ CF_2CFCH{=}CHCF_3 \end{array}$

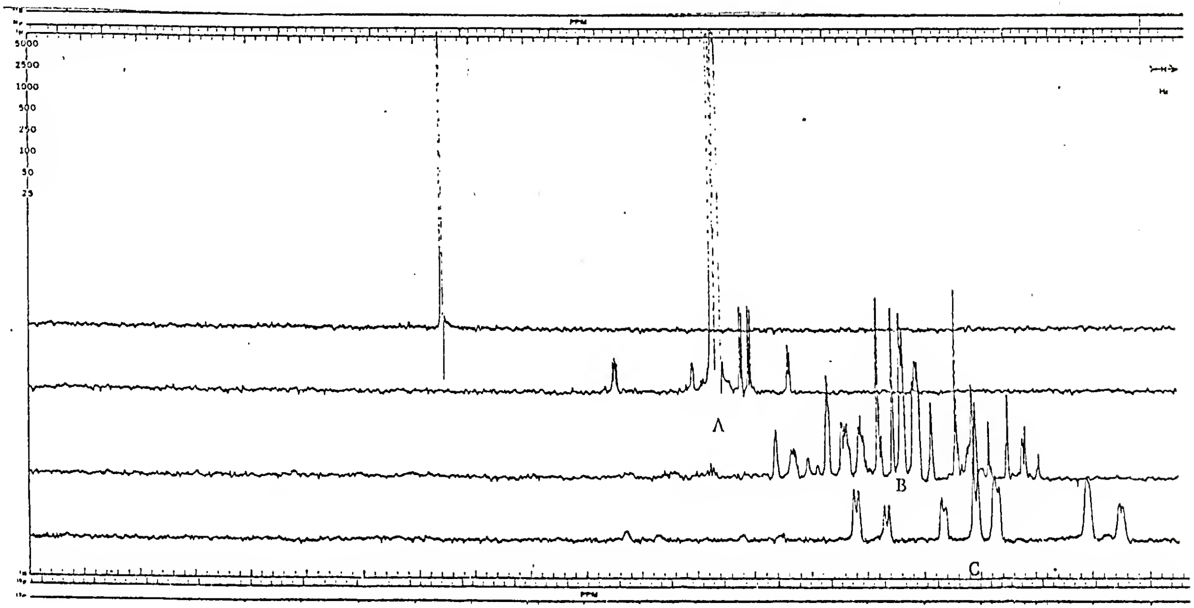
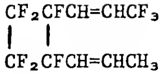


Figure 66 - F^{19} NMR of

$$\begin{array}{l}\text{B}\quad\;\;\text{C}\quad\;\;\text{A}\\ CF_2CFCH{=}CHCF_3\\ \;|\quad\;\;|\\ CF_2CFCH{=}CHCH_3\\ \text{B}\;\;\text{C}\end{array}$$

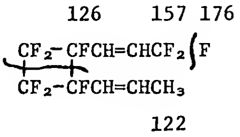
TABLE XXVII

MASS SPECTRUM OF



$$\begin{array}{l} CF_2CFCH{=}CHCF_3 \\ \;\;|\quad\;\; | \\ CF_2CFCH{=}CHCH_3 \end{array}$$

Molecular Weight 298. Listing of peaks with >1% base peak intensity along with M$^\oplus$ peak.



Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
298	0.1 M$^\oplus$	121	9.4
213	2.5	119	2.1
211	3.2	114	1.6
198	1.0	113	4.7
195	1.2	111	3.1
183	5.3	109	2.6
177	4.2	107	5.4
176	59.2	106	1.5
175	1.2	103	2.9
169	1.0	102	4.4
164	1.0	101	5.5
163	11.2	100	1.0
161	13.5	95	6.7
158	1.6	93	1.2
157	23.9	91	3.9
145	7.5	89	1.2
138	1.0	87	1.6
137	3.4	85	2.3
133	1.9	83	1.1
132	1.1	77	3.0
129	4.3	76	1.1
127	4.2	75	5.6
126	31.1	72	10.5
125	1.3	71	5.6
123	6.2	69	11.7
122	100.0		

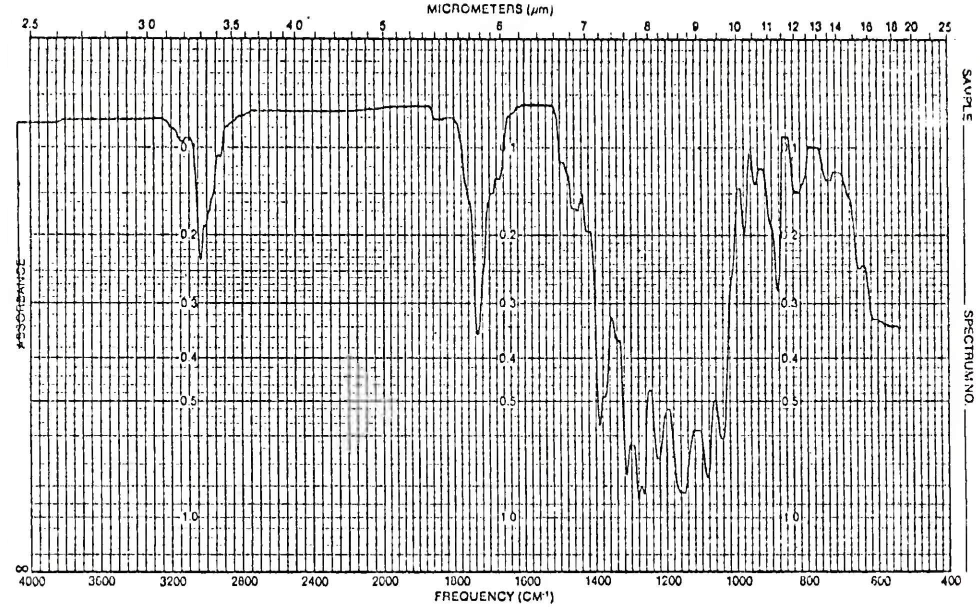
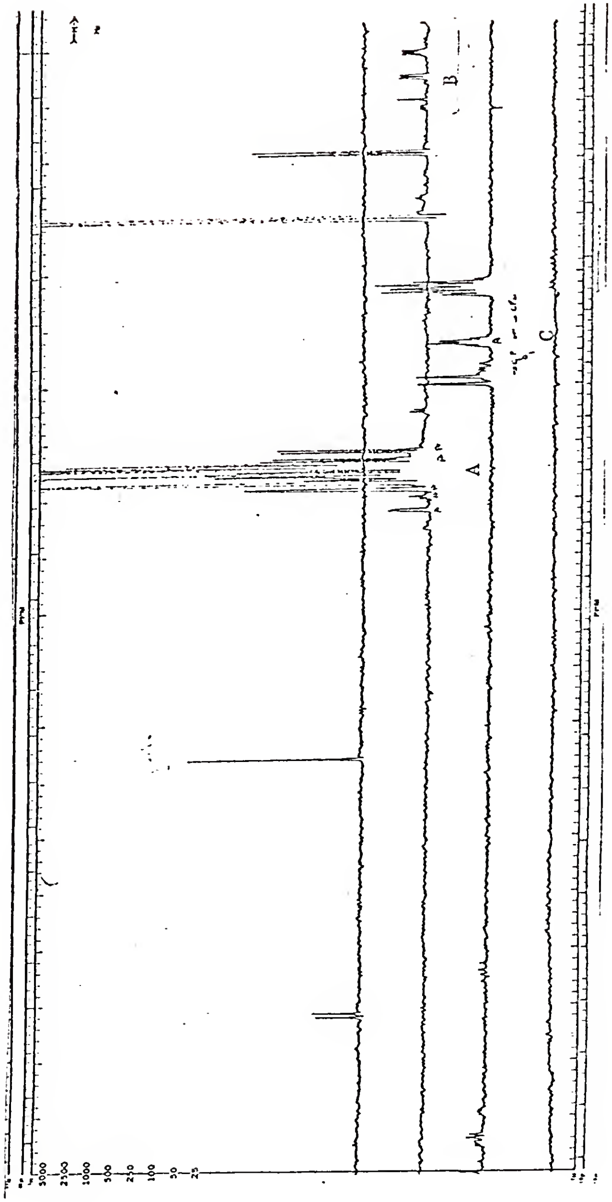
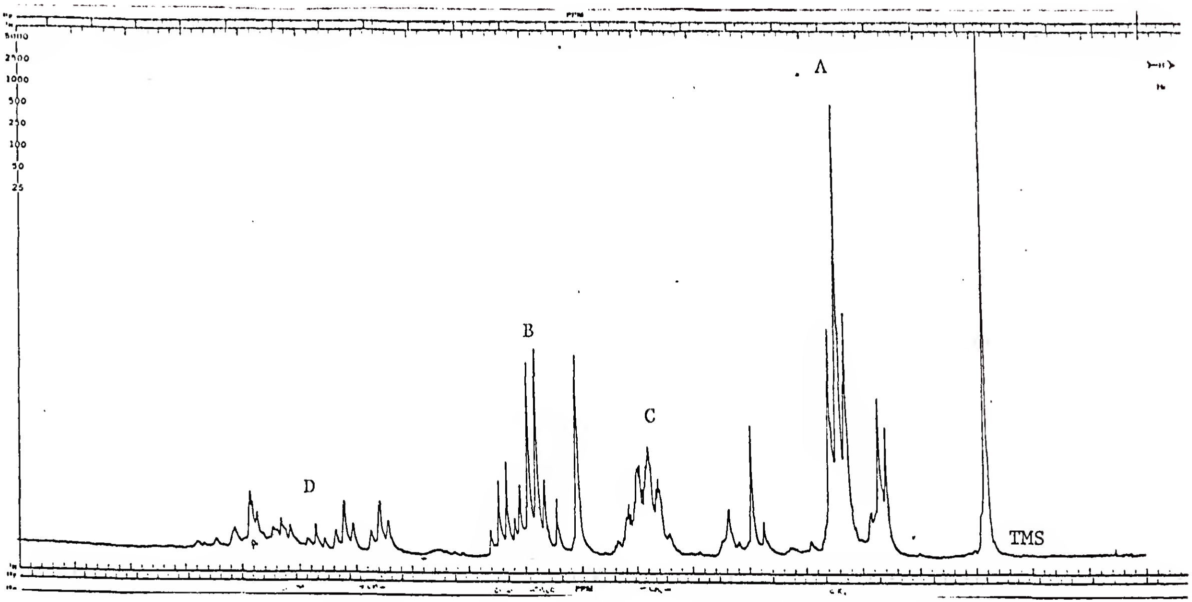


Figure 67 - Infrared Spectrum of $CF_3CH_2OCF_2CF{=}CHCH_2CF_3$ and $CH_3CH_2OCF_2CFHCH{=}CHCF_3$



B C A

Figure 68 - F^{19} NMR of $CH_3CH_2OCF_2CF{=}CHCH_2CF_3$



A B D C
Figure 69 - H^1 NMR of $CH_3CH_2OCF_2CF{=}CHCH_2CF_3$

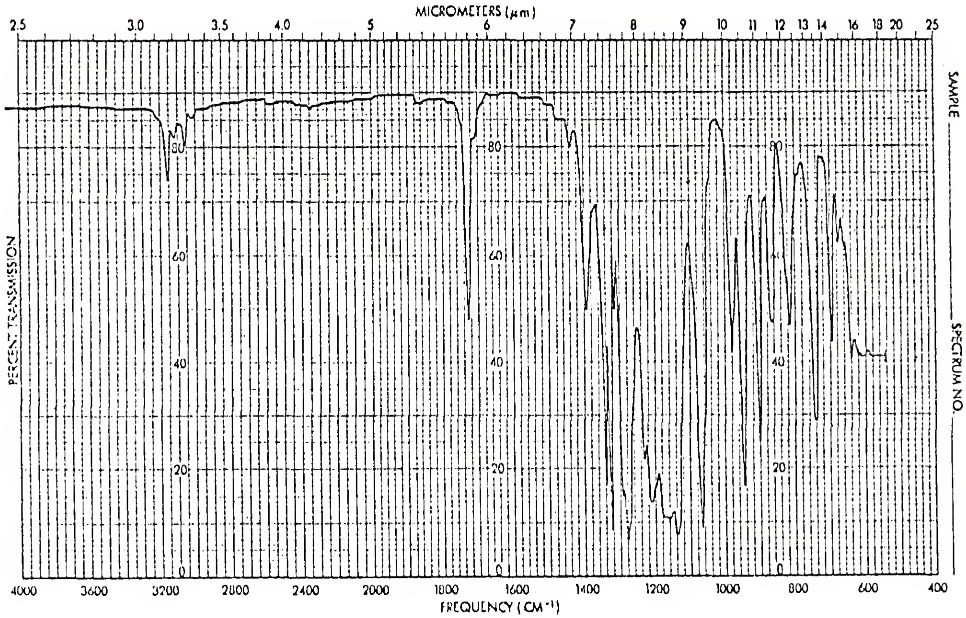


Figure 70 - Infrared Spectrum of $CF_2BrCF{=}CHCHBrCF_3$ (75%) and $CF_2BrCFBrCH{=}CHCF_3$ (25%)

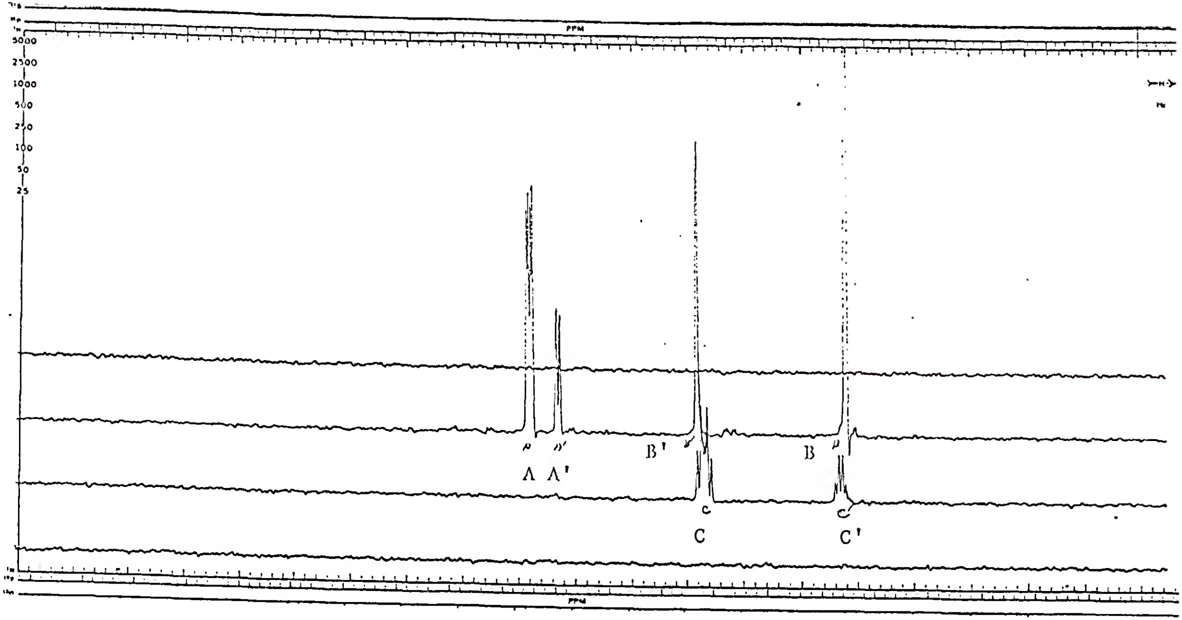
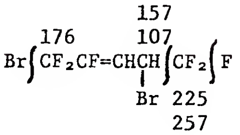


Figure 71 - F^{19} NMR of $\underset{A}{CF_2}Br\underset{C}{CF}{=}CH\overset{*}{C}HBr\underset{B}{CF_3}$ and $\underset{A'}{CF_2}Br\overset{*}{\underset{C'}{C}}FBrCH{=}CH\underset{B'}{CF_3}$

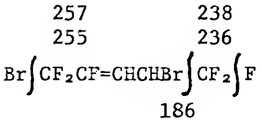
TABLE XXVIII

MASS SPECTRUM OF $CF_2BrCF{=}CHCHBrCF_3$ and $CF_2BrCFBrCH{=}CHCF_3$

Molecular Weight 336. Listing of all peaks >0.5% base intensity along with $M^{\oplus}$.



$$\mathrm{Br}\overset{176}{\int}\mathrm{CF_2CF{=}CH\underset{|\atop Br}{C}H}\overset{157\atop 107}{\underset{225\atop 257}{\int}}\mathrm{CF_2}\int\mathrm{F}$$



$$\mathrm{Br}\overset{257\atop 255}{\int}\mathrm{CF_2CF{=}CHCHBr}\overset{238\atop 236}{\underset{186}{\int}}\mathrm{CF_2}\int\mathrm{F}$$

Nominal Mass	% Int. Base
336	0.2 $M^{\oplus}$
258	6.1
257	96.9
256	6.2
255	100.0
238	7.7
237	2.4
236	7.7
235	2.4
217	0.7
215	0.5
211	1.0
207	8.0
205	7.8
193	2.7
191	3.1
188	2.5
186	2.6
185	0.5
177	3.3
176	60.0
175	4.2
173	1.3
163	1.5
162	0.5
161	4.3
160	0.5
158	0.8
157	13.0
156	1.7
155	3.5
[>5% Int. Base]	
137	5.9
131	6.5
129	6.7
126	64.1
113	30.1
107	10.0
106	6.5
95	5.4
88	5.5
75	14.4
69	27.5
57	26.4
56	6.8

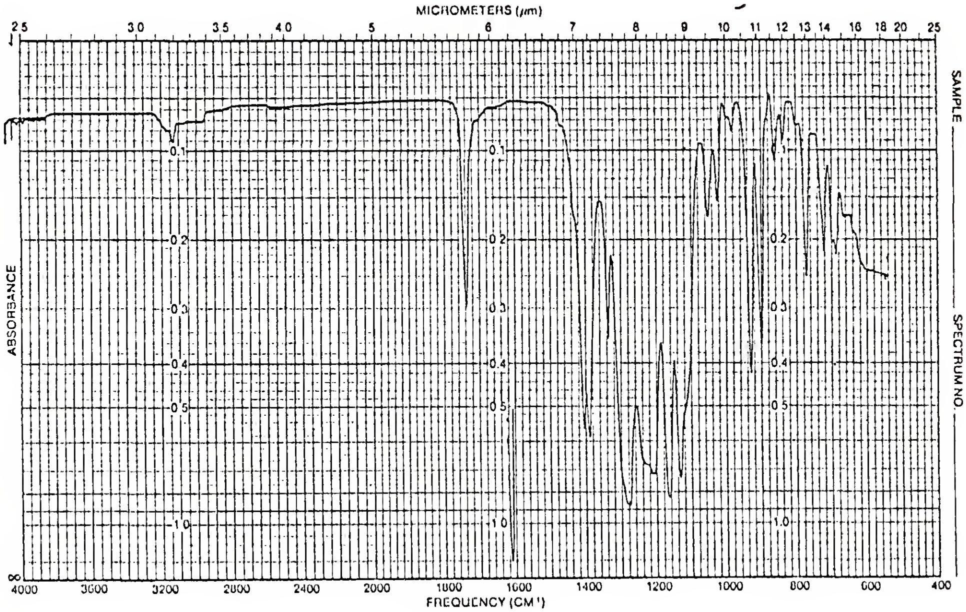
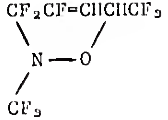


Figure 72 - Infrared Spectrum of



$CF_2CF{=}CHCHCF_3$, N—O, CF_3

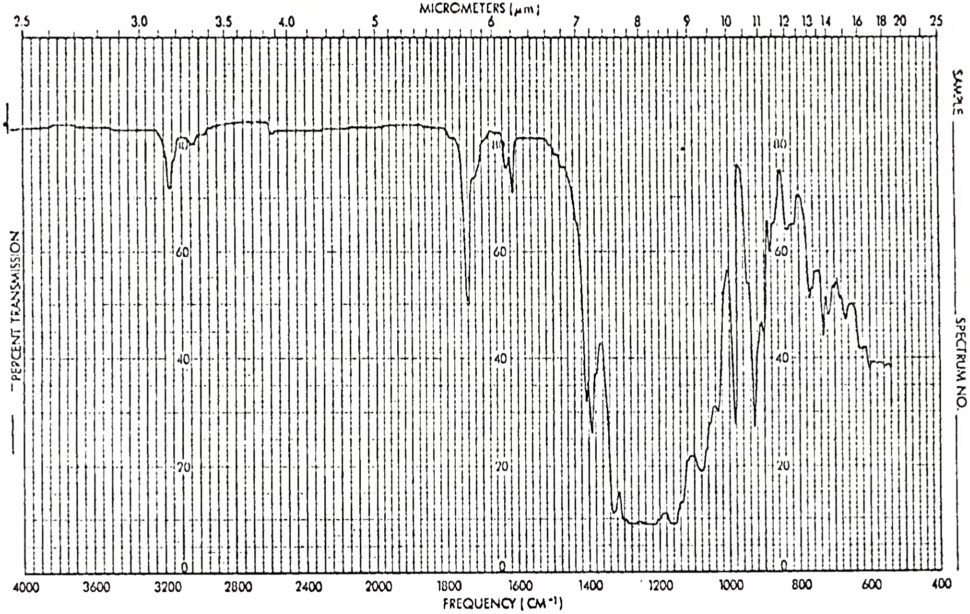


Figure 73 - Infrared Spectrum of Polymers of Reaction Between CF_3NO + CF_2=CFCH=$CHCF_3$

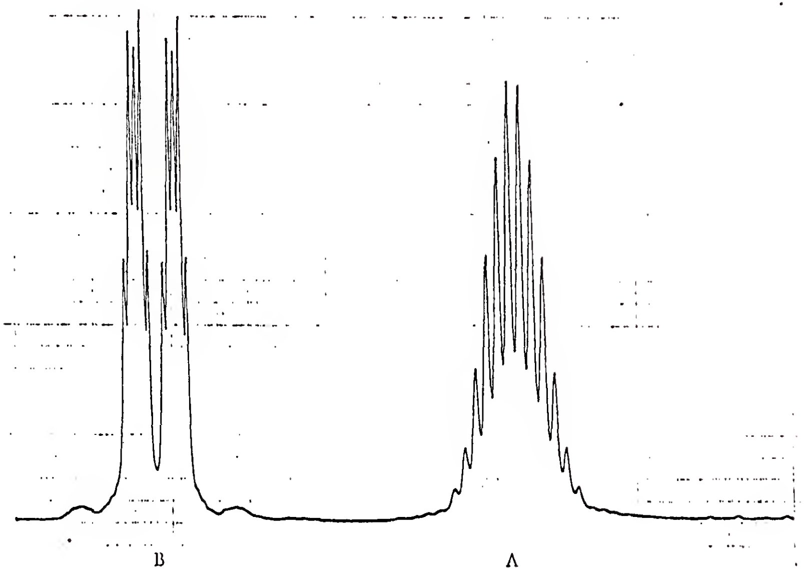
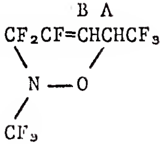


Figure 74 - H^1 NMR of



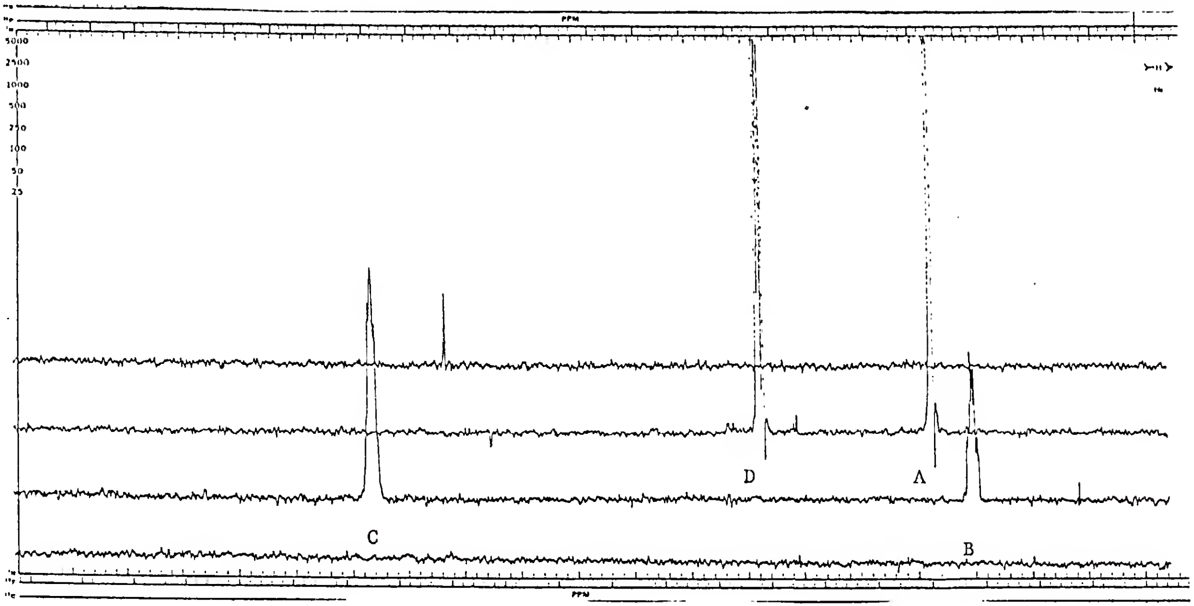


Figure 75 - F^{19} NMR of

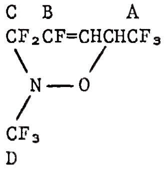
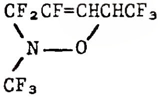
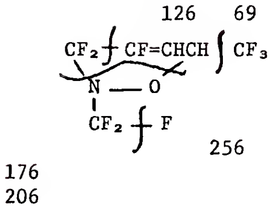


TABLE XXIX

MASS SPECTRUM OF $CF_2CF{=}CHCHCF_3$



Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
275	1.3 $M^{\oplus}$	96	1.0
256	4.6	95	4.1
206	12.4	91	2.5
177	5.4	75	4.2
176	100.0	72	1.6
168	1.0	70	1.0
158	1.2	69	62.3
157	5.9	57	5.0
156	6.0	51	1.9
145	6.9	50	1.4
140	1.1	45	1.9
130	2.9	44	3.5
127	1.8	43	1.4
126	40.2	32	4.3
125	1.1	31	2.8
123	2.2	30	2.7
118	4.4	29	4.7
114	2.7	28	18.4
113	1.3		
107	1.7		

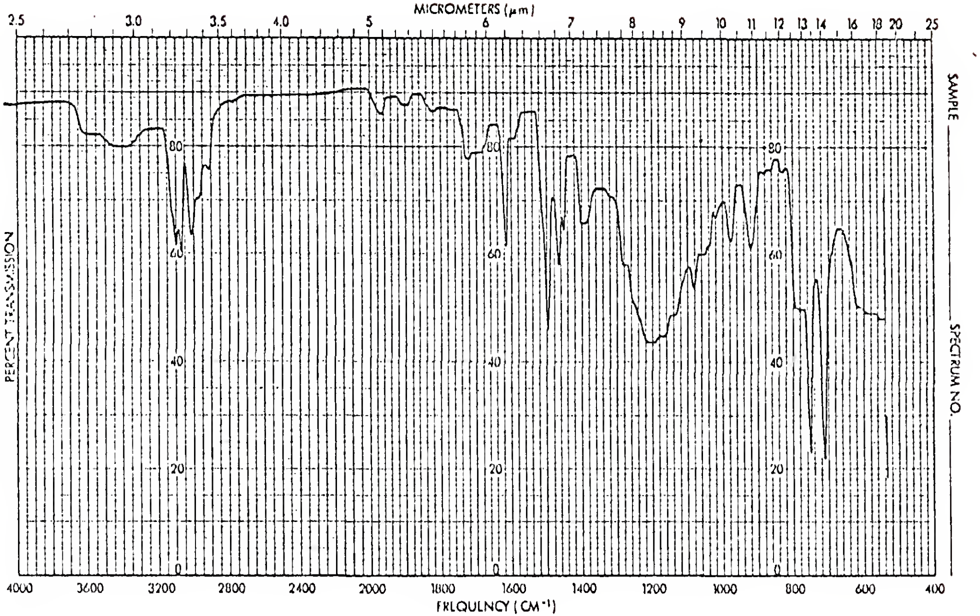
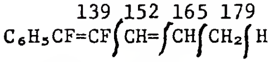


Figure 76 - Infrared Spectrum of $C_6H_5CF{=}CFCH{=}CHCH_3$

TABLE XXX

MASS SPECTRUM OF $C_6H_5CF{=}CFCH{=}CHCH_3$

Molecular Weight 180. Listing of all peaks >0.5% intensity base along with $M^{\oplus}$



$C_6H_5CF{=}CF\overset{139}{\int}CH{=}\overset{152}{\int}CH\overset{165}{\int}CH_2\overset{179}{\int}H$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
181	1.0	133	1.2
180	5.6 $M^{\oplus}$	129	1.4
179	3.1	128	4.0
178	2.3	127	3.2
177	0.6	126	2.1
166	0.9	122	11.4
165	6.4	121	7.6
164	1.5	119	1.1
163	0.6	118	6.7
161	0.5	117	3.4
160	1.9	115	5.6
159	0.8	109	1.2
158	0.7	107	5.2
157	0.5	105	4.3
156	1.4	104	1.1
155	13.0	103	2.7
154	100.0	102	3.4
153	40.9	101	1.9
152	27.5	95	1.2
151	7.8	94	7.0
150	2.3	91	3.3
149	0.5	89	2.4
146	1.3	87	1.3
145	5.6	79	2.9
[>1% Int. Base]		78	3.6
139	1.8	77	11.8

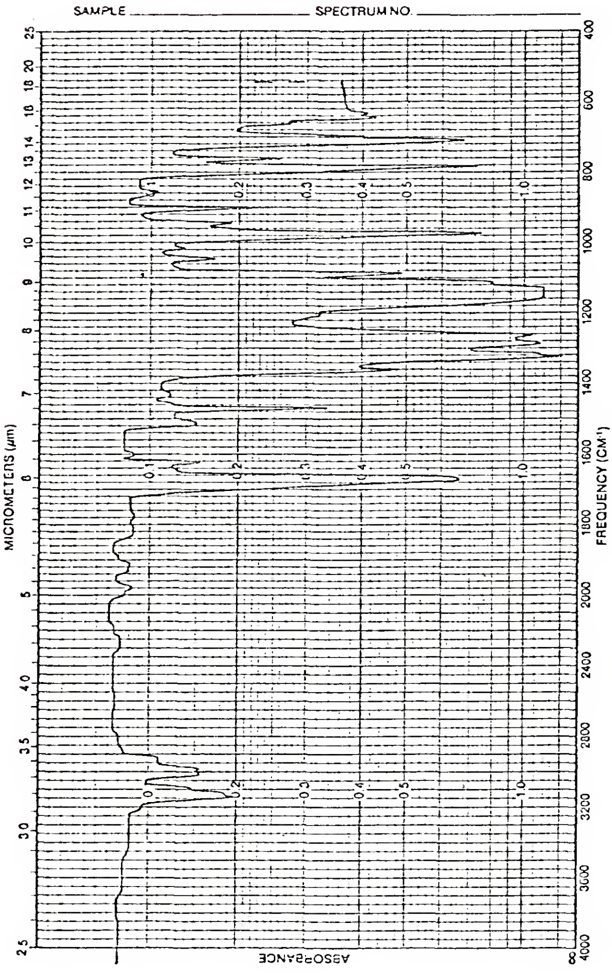


Figure 77 - Infrared Spectrum of $C_6H_5CF=CFCH=CHCF_3$

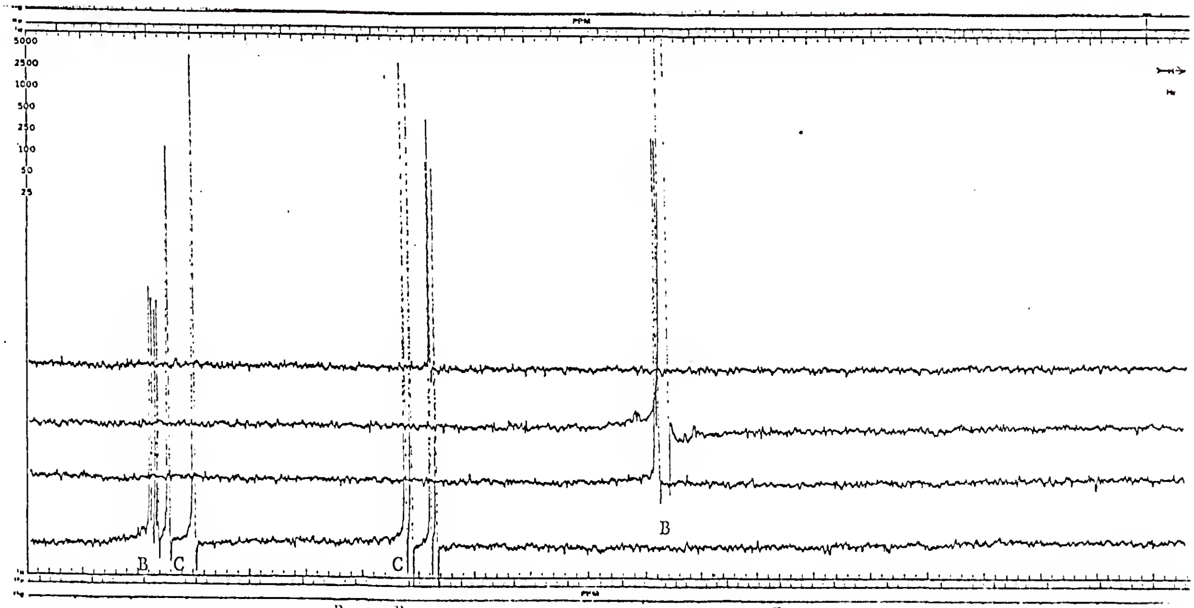
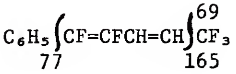


Figure 78 - F^{19} NMR of $C_6H_5\overset{\overset{B}{F}\diagdown}{C}=\overset{\overset{B}{F}/}{C}CH=CH\overset{A}{CF_3}$ Cis and $C_6H_5\underset{/\underset{C}{F}}{C}=\overset{\overset{C}{F}/}{C}CH=CH\underset{A}{CF_3}$ Trans

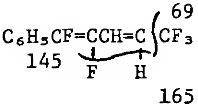
TABLE XXXI

MASS SPECTRUM OF $C_6H_5CF=CFCH=CHCF_3$

Molecular Weight 234. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$\underset{77}{C_6H_5}\,\Big(CF=CFCH=CH\Big)\,\underset{165}{\overset{69}{CF_3}}$



$\underset{145}{C_6H_5}CF=\underset{F\quad H}{CCH=C}\,\Big(\underset{165}{\overset{69}{CF_3}}$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
235	5.4	152	3.2
234	46.6 $M^{\oplus}$	151	5.8
219	1.8	146	7.6
215	5.2	145	25.6
214	2.0	144	2.9
213	6.8	143	2.8
195	5.4	138	2.1
193	1.5	133	4.1
183	1.9	127	3.4
182	2.8	125	3.7
175	1.1	115	9.9
169	2.9	82	5.4
166	10.4	77	3.1
165	100.0	75	3.8
164	48.9	69	3.6
163	4.7	63	3.2
162	1.0	57	7.5
155	1.3	51	5.1
154	9.9	32	5.8
153	3.8	28	29.8

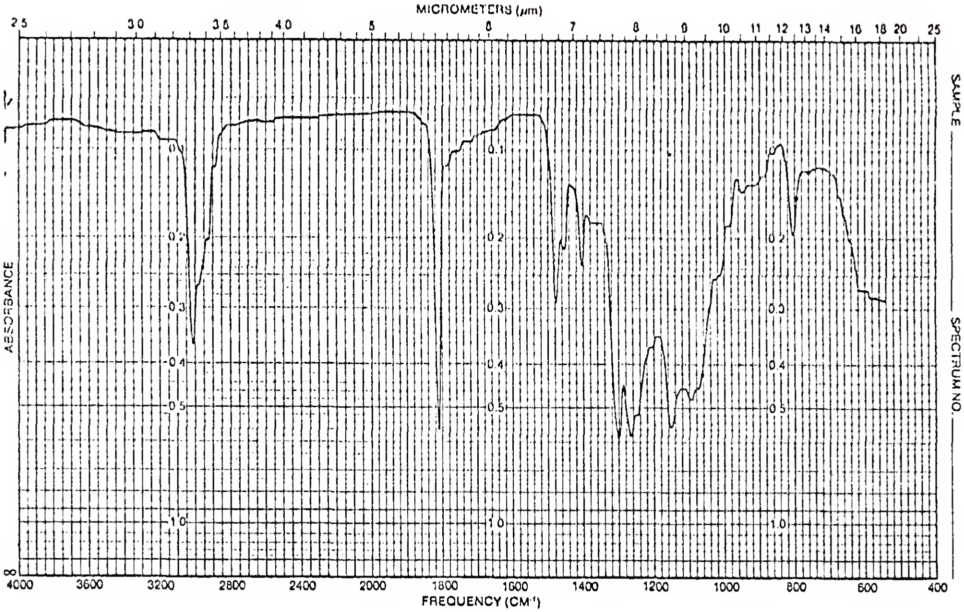


Figure 79 - Infrared of $\begin{array}{l}CF_2{=}CFCH_2CHCH_3\\ \qquad\qquad\quad\ |\\ CF_2{=}CFCH_2CHCH_3\end{array}$

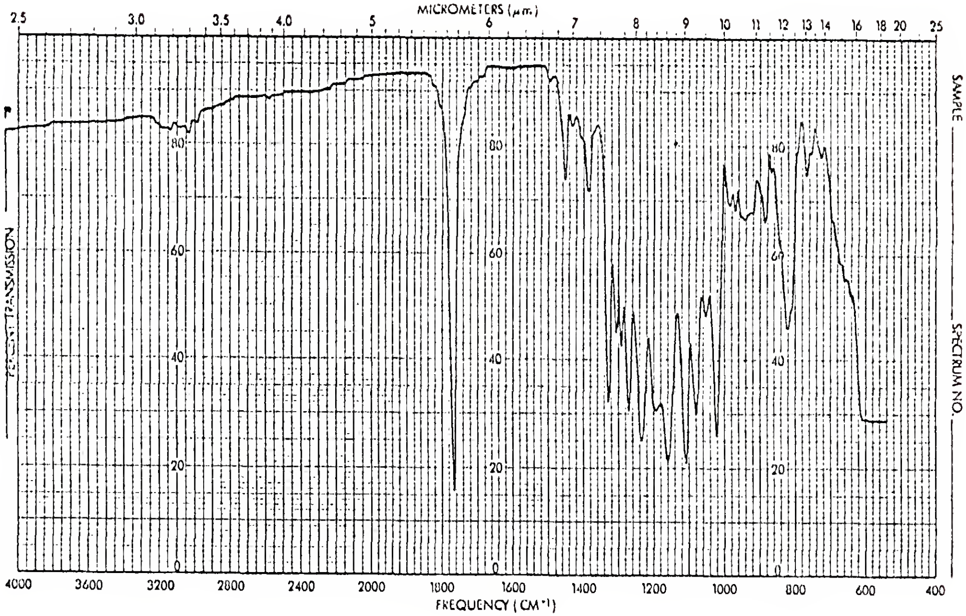


Figure 80 - Infrared Spectrum of $CF_2ClCFClCH_2CH=CF_2$

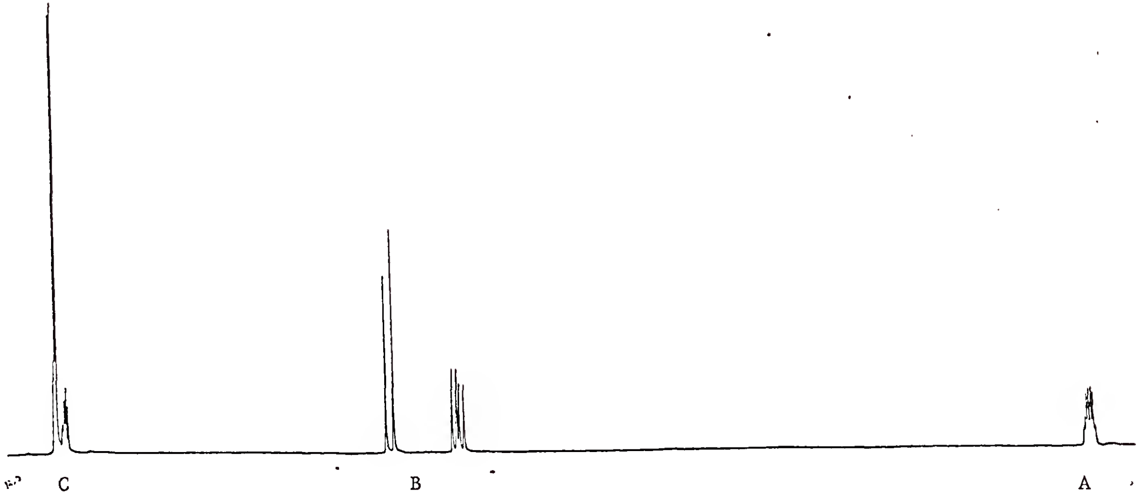
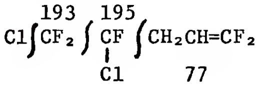


Figure 81 - F^{19} NMR of $\underset{C}{CF_2}Cl\underset{A}{CF}ClCH_2CH=\underset{B}{CF_2}$

TABLE XXXII

MASS SPECTRUM OF $CF_2-ClCFClCH_2CH=CF_2$

Molecular Weight 230. Listing of peaks with >1% base peak intensity along with $M^{\oplus}$ peak.



$$Cl \int CF_2 \overset{193}{\int} \underset{Cl}{\overset{195}{CF}} \int \underset{77}{CH_2CH=CF_2}$$

Nominal Mass	% Int. Base	Nominal Mass	% Int. Base
230	2.1 $M^{\oplus}$	95	16.1
228	3.3	93	5.9
195	1.3	89	1.0
193	4.4	88	1.3
177	1.2	87	4.0
175	1.1	85	10.9
173	3.2	78	3.3
163	2.4	77	100.0
157	2.4	75	4.3
145	2.4	73	1.3
143	7.0	69	5.6
137	1.6	67	2.7
131	1.2	64	1.0
129	3.2	58	1.3
127	3.9	57	5.1
123	1.2	51	14.8
116	1.2	45	1.3
113	4.6	44	1.1
111	6.0	43	3.6
108	3.5		
107	1.4		
101	1.0		

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BIOGRAPHICAL SKETCH

Jerry Ronald Patton was born March 16, 1946, in Comanche, Texas. After moving to Arcadia, Florida, at the age of two, he attended public school in Arcadia, where he graduated from DeSoto County High School in June, 1964.

He attended the University of Florida where he received his Bachelor of Science degree in June, 1968. Mr. Patton went to work with PCR, Incorporated, in July, 1968, working in research with high density damping fluids. After gaining experience in silicone and fluorocarbon chemistry, Mr. Patton entered graduate school at the University of Florida in 1972, while continuing to work for PCR, Incorporated. Upon receiving his Masters of Science degree in June, 1974, he continued his employment and started advance studies toward a Ph.D. degree.

Mr. Patton is married to the former Jonnett Gumm of West Virginia and has a daughter, Brandi, and a son, Brian.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Paul Tarrant

Paul Tarrant, Chairman
Professor of Chemisty

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George B. Butler

George B. Butler
Professor of Chemisty

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W. S. Brey, Jr.
Professor of Chemisty

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Professor of Chemisty

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate Council, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1980

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